

# **FERRO2003**

Fundamental Physics of Ferroelectrics

2-5 February 2003

Williamsburg, Virginia

**Sponsored by the Office of Naval Research**

*Welcome to Williamsburg.*

## NOTES

# PROGRAM

## SUNDAY, FEBRUARY 2, 2003

17:00-19:00	Registration and Welcoming Reception	Woodlands Center
19:00-20:30	Dinner	

## MONDAY, FEBRUARY 3, 2003

08:00-08:30	Registration	Woodlands Center
08:30-08:40	Welcome	
<b>Session 1</b>	<b>H. Krakauer, Chair</b>	
08:40-09:15	<b>R.E. Cohen</b> , M. Sepiarsky and Z. Wu	Towards accurate first-principles simulations of large strain piezoelectric transducer materials
09:15-09:50	<b>I. Grinberg</b> and A.M. Rappe	Ab Initio studies of silver based ferroelectrics
09:50-10:25	<b>L. Bellaiche</b>	Properties of piezoelectric materials from First Principles
10:25-10:40	Coffee	
10:40-11:15	<b>E. Furman</b> , C.A. Randall and I.M. Reaney	Morphotropic boundaries in high temperature ferroelectrics
11:15-11:30	<b>J. Íñiguez</b> , D. Vanderbilt and L. Bellaiche	First-principles study of $(1-x)\text{BiScO}_3\text{-}x\text{PbTiO}_3$ piezoelectric alloys
11:30-12:05	<b>P.M. Gehring</b> , G. Shirane and Z.-G. Ye	PMN-10%PT is not rhombohedral
12:05-13:15	Lunch	Woodlands Center
<b>Session 2</b>	<b>D. Vanderbilt, Chair</b>	
13:15-13:35	<b>T. Egami</b> , W. Dmowski and E. Mamontov	Temperature and composition dependence of the local environment of Pb containing relaxor systems
13:35-13:50	<b>J. Hlinka</b> , S. Kamba, J. Kulda, J. Petzelt, C.A. Randall and S. Zhang	What do we learn from diffuse scattering in cubic relaxor ferroelectrics
13:50-14:25	<b>B.P. Burton</b> , E. Cockayne, S. Prosandeev and U. Waghmare	Large scale simulations of the relaxor ferroelectric $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ with chemical order-disorder and Pb-O vacancy pairs: a first principles effective Hamiltonian study
14:25-15:00	<b>A. Van der Ven</b> , A. Predith and G. Ceder	Phase diagrams and diffusion in multicomponent oxides from first principles
15:00-15:15	S. Halilov, M. Fornari and <b>D.J. Singh</b>	First principles investigation of novel ferroelectric perovskite alloys based on A-site substitution
15:15-15:35	Coffee	
15:35-15:55	<b>J.B. Neaton</b> , U.V. Waghmare, N. A. Hill and K. M. Rabe	First-principles study of multiferroism in $\text{BiFeO}_3$
15:55-16:15	<b>J. Wang</b> , M. Wuttig and R. Ramesh	Epitaxial $\text{BiFeO}_3$ Multiferroic thin film heterostructures
16:15-16:35	<b>N.A. Spaldin</b> , A. Filippetti and C. Schelle	A new mechanism for ferroelectricity and a new ferroelectric with an old mechanism
16:35-17:10	<b>P. Ghosez</b> and J. Junquera	Thickness-dependence of the ferroelectric properties in perovskite ultrathin film
17:10-17:30	<b>H. Hellwig</b> , R. J. Hemley, R. E. Cohen and D. Rytz	Micro-Brillouin investigations on relaxor ferroelectrics
17:30-18:05	<b>D. Viehland</b> , J.-F. Li, and A.G. Khachatryan	Role of microtwins in poled oriented single crystals of PMN-PT
18:30-19:30	Dinner	Woodlands Center
19:30-21:30	Poster Session	Woodlands Center

## NOTES

# POSTERS

<b>P1</b>	A.R. Akbarzadeh and L. Bellaiche	Quantum effects in incipient ferroelectrics $\text{KTaO}_3$ and $\text{K}(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$
<b>P2</b>	A. Al-barakaty and L. Bellaiche	Finite-temperature properties of $\text{Pb}(\text{Sc}_{(1-x)/2}\text{Nb}_{(1-x)/2}\text{Ti}_x\text{O}_3$ solid solution near its morphotropic phase boundary
<b>P3</b>	A.S. Al-Hawery	Curie temperature of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ceramics
<b>P4</b>	I.T. Bodnar	Oscillations of refractive indices near the phase transitions in $(\text{Ba},\text{Na})\text{NbO}_3$ crystal
<b>P5</b>	I.T. Bodnar and A.U. Sheleg	Refractive indices, dispersion and thermo-optical coefficients of KTP crystal
<b>P6</b>	R. Caracas and X. Gonze	First-principles simulations of $\text{K}_2\text{SeO}_4$ dielectrics
<b>P7</b>	C. Caracas, K. Rabe and X. Gonze	Automatic generation of lattice Wannier functions
<b>P8</b>	V.R. Cooper, I. Grinberg and A.M. Rappe	Empirical modeling of complex oxides: the bond valence approach
<b>P9</b>	R.I. Eglitis, E.A. Kotomin, G. Borstel and V.S. Vikhnin	Quantum chemical modeling of polarons and excitons in $\text{ABO}_3$ perovskites
<b>P10</b>	A.M. George, J. Íñiguez and L. Bellaiche	Effects of atomic short range order on the properties of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ alloy near its morphotropic phase boundary
<b>P11</b>	I. Grinberg and A.M. Rappe	Local structure in lead based ferroelectrics by DFT calculations
<b>P12</b>	E. Heifets, R.I. Eglitis, E.A. Kotomin, J. Maier, and G. Borstel	Ab initio calculations of the polar surface structure for $\text{SrTiO}_3$ perovskite
<b>P13</b>	P. Juhás, W. Dmowski, T. Egami, I. Grinberg, A. M. Rappe and P.K. Davies	Local structure – properties relations in the $(1-x)\text{Pb}(\text{Sc}_{2/3}\text{W}_{1/3})\text{O}_3 - (x)\text{Pb}(\text{Ti/Zr})\text{O}_3$ relaxors
<b>P14</b>	I. Kornev and L. Bellaiche	Finite-temperature properties of PZT superlattices near the morphotropic phase boundary from first principles
<b>P15</b>	D. La-Orauttapong, J. Toulouse, B. Hennion, W. Chen, Z.-G. Ye, R. Erwin and J.L. Robertson	Phonon anomaly of the relaxor ferroelectric $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ by neutron inelastic scattering
<b>P16</b>	J.Y. Li and N. Rao	Giant electrostriction in ferroelectric polymer based composites
<b>P17</b>	G. Malovichko and V. Grachev	Point defects and physical properties of ferroelectrics: lithium niobate
<b>P18</b>	D. Mao, H. Krakauer and M. Wu	Calculated electric field gradients in tetragonal and monoclinic PZT
<b>P19</b>	M. Manu, Y. Wu, R. Resta and R. Car	Car-Parrinello molecular dynamics with Wannier functions
<b>P20</b>	J. Ouyang, V. Nagarajan, A. Roytburd and R. Ramesh	Nanoscale effects in PZT thin films by piezo-response studies
<b>P21</b>	S.A. Prosandeev, Eric Cockayne and B. P. Burton	First principles calculations of lattice dynamics in some $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ supercells
<b>P22</b>	I.P. Raevski, S.A. Prosandeev, S.M. Emelyanov, V.G. Smotrakov, V.V. Eremkin, F.I. Savenko, I.N. Zakharchenko, E.S. Gagarina, O.A. Bunina, and E.V. Sahkar	Cation ordering in single crystals of 1:1 and 1:2 complex perovskites solid solutions
<b>P23</b>	V. Ranjan, N. Farrer, L. Bellaiche and E.J. Walter	Properties of hexagonal $\text{ScN}$ from first-principles
<b>P24</b>	N. Sai, J. Anderson and A.M. Rappe	A Site substitution and local structure in ferroelectric perovskites
<b>P25</b>	E. Şentürk and F. Mikailov	Non-Debye type relaxator study with Cole-Cole plots in $\text{Sr}_{0.61-x}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6\text{Ce}_x$ ( $x=0, 0.0066$ )
<b>P26</b>	S. Tinte, K. Rabe and D. Vanderbilt	Anomalous enhancement of tetragonality by negative pressure in $\text{PbTiO}_3$
<b>P27</b>	C.-S. Tu, L.-W. Huang, V.H. Schmidt and R. Chien	Phase transformation vs. monoclinic rotations in $\langle 102 \rangle$ -cut PMN-PT crystal
<b>P28</b>	M. Veithen, Ph. Ghosez and X. Gonze	First-principles study of the electrooptic effect in ferroelectric oxides
<b>P29</b>	Z. Wu, R.E. Cohen and D.J. Singh	Weighted density approximation (WDA) calculations for ferroelectric materials

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## TUESDAY, FEBRUARY 4, 2003

<b>Session 3</b>	<b>G. Samara, Chair</b>	
08:30-09:05	<b>R. Blinc</b> and B. Zalar	NMR evidence for the coexistence of order-disorder and displacive components in barium titanate and strontium titanate
09:05-09:40	W.-H. Chan, J. Zhai, Z.K. Xu, <b>H. Chen</b> and E.V. Colla	Temporal effects in dielectric properties of some antiferroelectric complex perovskites
09:40-09:55	<b>S.A. Prosandeev</b> , I.P. Raevski and U. Waghmare	Diffusive phase transitions in ferroelectrics and antiferroelectrics
09:55-10:10	Coffee	
10:10-10:45	<b>J. Toulouse</b> , D. La-Orauttapong and O. Svitelskiy	Condensation and slow dynamics of polar nanoregions in PMN, PZN and PZN-PT
10:45-11:00	<b>V.H. Schmidt</b> , R. Chien, I.-C. Shih and C.-S. Tu	Polarization rotation and monoclinic phase in relaxor ferroelectric PMN-PT crystal
11:00-11:15	<b>A. Tkachuk</b> and H. Chen	Structural synchrotron x-ray studies of anti-ferrodistortive nanodomains in PMN relaxor
11:15-11:30	<b>S.B. Vakhrushev</b> , A. Naberezhnov, N.M. Okuneva, B. Dorner, A.Ivanov, B. Dkhil, J.-M. Kiat and A. Kholkin	Topology of polar nanoregions in relaxor ferroelectrics
11:30-12:05	<b>M.B. Weissman</b> , E.V. Colla and L.K. Chao	Noise and aging studies of relaxor ferroelectrics
12:05-13:15	Lunch	Woodlands Center
<b>Session 4</b>	<b>R. Cohen, Chair</b>	
13:15-13:50	E.L. Venturini, <b>G.A. Samara</b> , M. Itoh and W. Kleemann	Pressure as a probe of the physics of compositionally-substituted quantum paraelectrics: $\text{SrTiO}_3$
13:50-14:25	<b>W. Kleemann</b> , J. Dec, R. Wang, M. Itoh, and R. Pankrath	Domain states in uniaxial relaxors and quantum ferroelectrics
14:25-15:00	<b>E. Salje</b>	Particle transport along domain walls: superhighways or parking lanes?
15:00-15:20	Coffee	
15:20-15:35	<b>L. He</b> and D. Vanderbilt	First-principles study of oxygen vacancy pinning of domain walls in $\text{PbTiO}_3$
15:35-15:50	<b>I. Naumov</b> , K. Rabe and M. Cohen	Impact of antiphase domain boundaries on the dielectric response of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ Thin Films
15:50-16:25	<b>W. Cao</b> and J. Erhart	Theoretical analysis of domain engineering method
16:25-16:40	<b>Y.L. Li</b> , S. Choudhury, S.Y. Hu, Z.K. Liu, and L.Q. Chen	Computer simulation of domain stability and domain structures in ferroelectric thin films
16:40-16:55	C. Bungaro and K.M. Rabe	Lattice instabilities and dielectric response of nanostructured ferroelectrics
16:55-17:10	<b>E. Cockayne</b> , B.P. Burton and U. Waghmare	First principles effective Hamiltonians for relaxor ferroelectrics: distinct local variables for each cation species
18:30-21:30	Conference Dinner	Kings Arms Tavern

## NOTES



## WEDNESDAY, FEBRUARY 5, 2003

<b>Session 5</b>	<b>L. Bellaiche, Chair</b>	
08:30-09:05	<b>J.F. Scott</b>	Ferroelectric Nanotubes
09:05-09:25	<b>P. Umari</b> and A. Pasquarello	Ab-Initio molecular dynamics in a finite homogeneous electric field
09:25-09:40	<b>H. Fu</b> and L. Bellaiche	First-principles calculations of piezoelectric response under finite electric fields
09:40-09:55	<b>A. Antons</b> , J.B. Neaton and D. Vanderbilt	First-principles study of intrinsic dielectric loss [in oxides] at microwave frequencies
09:55-10:15	P. Sen, L.K. Wagner, J.W. Lee, M. Bajdich and <b>L. Mitás</b>	Electronic structure of perovskite transition metal oxides by quantum Monte Carlo approaches
10:15-10:30	Coffee	
10:30-10:50	<b>H. Krakauer</b> and S. Zhang	Quantum Monte Carlo method using phase-free random walks with Slater determinants
10:50-11:05	<b>M. Sepliarsky</b> and R.E. Cohen	Atomistic model potential for PbTiO <sub>3</sub> fitted to LDA and GGA first-principles results
11:05-11:20	<b>R.I. Eglitis</b> , D. Fuks, S. Dorfman, E.A. Kotomin, G. Borstel and V.A. Trepakov	Quantum chemical modeling of phase transitions in perovskite solid solutions
11:20-11:35	<b>V. Srinivasan</b> , R. Gebauer, R. Resta, and R. Car	PbTiO <sub>3</sub> at finite temperature: an ab-initio molecular dynamics study
11:35-11:50	<b>D.H. Zhou</b> , G.L. Hoatson, W.J. Brouwer and R.L. Vold	Multinuclear single and multiple quantum MAS NMR studies of perovskite relaxor ferroelectrics
11:50-12:15	Discussion	
12:30-13:45	Lunch	Woodlands Center

## NOTES

# ABSTRACTS

## NOTES

**Finite-temperature properties of  $\text{Pb}(\text{Sc}_{(1-x)/2}\text{Nb}_{(1-x)/2}\text{Ti}_x\text{O}_3$   
solid solution near its morphotropic phase boundary**

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A first-principle-derived approach is developed and used to study the structural finite-temperature properties of  $(1-x)\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3 + x\text{PbTiO}_3$  (PSN-PT) for  $Ti$  composition ranging between 40% and 55%. At 50K, PSN-PT is predicted to adopt a ferroelectric tetragonal phase for  $x \geq 43\%$ , and a ferroelectric rhombohedral structure for  $x < 41\%$ . Our most important results are related to the compositions ranging in between 41% and 43%. More precisely, our calculations point out that for these composition: (1) there are intermediate monoclinic phases (2) the monoclinic phases associated with a PM and a CM space group are very close to each other in free energy, and (3) a minor change of atomic distribution and/or a slight modification in composition can alter the space group of the monoclinic ground-state. Items (2) and (3) make the morphotropic phase boundary of PSN-PT results unique. Microscopic effects responsible for these items will also be discussed.

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# Quantum effects in incipient ferroelectrics $\text{KTaO}_3$ and $\text{K}(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$

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We study the incipient ferroelectrics  $\text{KTaO}_3$  and  $\text{K}(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$ , using a parameterized effective Hamiltonian ( $H_{\text{eff}}$ ). Quantum effects are turned off and on by performing classical Monte-Carlo and Path-integral Monte-Carlo simulations respectively, both using the energy provided by  $H_{\text{eff}}$ . We find that the fitting of all the  $H_{\text{eff}}$  parameters within the local density approximation (LDA) yields a theoretical dielectric constant of  $\text{KTaO}_3$  that is much smaller than the experimental one. This suggests that LDA is inadequate in  $\text{KTaO}_3$  and  $\text{K}(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$  with small Nb concentrations. On the other hand, allowing the deviation of only one parameter of  $H_{\text{eff}}$  with respect to its LDA value leads to an excellent agreement over a wide temperature range between theory and experiment for the dielectric constant of  $\text{KTaO}_3$ . In particular, Path-integral Monte-Carlo simulations show a plateau with a height of  $\approx 4000$  below 10 K. Interestingly, using this second set of  $H_{\text{eff}}$  parameters leads to the prediction that  $\text{KTaO}_3$  is classically ferroelectric while being paraelectric once quantum effects are included. (Note that the LDA-fitted  $H_{\text{eff}}$  produces different qualitative results in the sense that it has a paraelectric ground state *both* at the classical and quantum levels). In other words, our second set of  $H_{\text{eff}}$  parameters predicts that quantum fluctuations suppress the paraelectric-to-ferroelectric phase transition. Our simulations also provide details of the microscopic picture associated with this suppression. Finally, simulations indicating how  $\text{K}(\text{Ta}_{1-x}\text{Nb}_x)\text{O}_3$  becomes ferroelectric when inserting a very small amount of Nb atoms will be presented and discussed, if time allows.

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## **Curie Temperature of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ Ceramics**

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The Gouy balance technique has been employed to determine the Curie temperature ( $T_c$ ) of  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  ceramics. The variation of magnetization with different concentration has been examined. We found the Curie temperature dependence of concentration.

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# First-principles study of intrinsic dielectric loss [in oxides] at microwave frequencies

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Ceramic dielectric materials play an important role in microwave communication systems such as cellular phones. One of the most important requirements for such materials, along with a high and weakly temperature-dependent dielectric constant, is a low dielectric loss. Unfortunately, first-principles calculations of dielectric loss at microwave frequencies are still in their infancy. Building on previous efforts[1], we demonstrate the feasibility of a fully first-principles approach to computing dielectric loss at microwave frequencies by focusing on the intrinsic losses which arise from anharmonic processes within the crystal, while neglecting extrinsic mechanisms associated with defects such as vacancies, impurity phases, and grain boundaries. Using SrO as our model system, we have computed the loss arising from two-phonon processes using third order force-constant matrices, phonon dispersion relations, phonon eigenvectors, and Born effective charges calculated from first principles using density-functional perturbation theory techniques. Progress in extending the work to SrTiO<sub>3</sub> will also be discussed.

[1] E.J. Wu and G. Ceder, J. Appl. Phys. **89**, 5630 (2001)

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## Properties of Piezoelectric Materials from First Principles

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*Ab-initio* approaches are developed and/or used to conduct different studies in various piezoelectric materials. Examples of these studies are: (1) the investigation of structural, dielectric and piezoelectric properties in perovskite solid solutions — either in their disordered forms or exhibiting long-range or short-range atomic ordering — near their morphotropic phase boundary; (2) the prediction of ferroelectric properties in vacancy-rich perovskite systems; (3) the simulation of quantum effects in incipient ferroelectrics; (4) the computation of ferroelectric properties in low-dimensional perovskite compounds; (5) the design of non-perovskite materials with large electromechanical responses. These studies lead to many striking, fundamental and technologically-useful features that will be revealed and discussed.

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Done in collaboration with Alirezea Akbarzadeh (UA), Abdullah Al-Barakaty (UA), Horace Crogman (UA), Nicholas Farrer (UA), Huaxiang Fu (UA), Aaron George (UA), Jorge Íñiguez (Rutgers University), Igor Kornev (UA), Kevin Leung (Sandia National Laboratories), Robert Sean Nichols (UA), Vivek Ranjan (UA), David Sichuga (UA), David Vanderbilt (Rutgers University), and Eric Walter (College of William and Mary)

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# NMR Evidence for the Coexistence of Order-Disorder and Displacive Components in Barium Titanate and Strontium Titanate

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The ferroelectric phase transition in  $\text{BaTiO}_3$  and the structural transition in  $\text{SrTiO}_3$  are generally considered to be the classical examples of displacive soft mode type phase transitions describable by anharmonic lattice dynamics. The question of the possible existence of a displacive to order-disorder cross-over close to the phase transition temperatures is however still open. The problem to be solved is whether the potential for the Ti motion in the cubic paraelectric phase exhibits a minimum at the center of the oxygen cage or whether the Ti ion is disordered between several off-center sites. Since the electric field gradient (EFG) tensor is zero by symmetry at the central and non-zero at the off-center sites, the above problem could be definitely solved by quadrupole perturbed Ti NMR. Here we report on the first observation of a quadrupole coupling induced  $^{47}\text{Ti}$  and  $^{49}\text{Ti}$  satellite background in the cubic phase both in barium titanate and in strontium titanate which transforms into well defined satellite lines below  $T_C$ . The angular dependence of the second moments in the cubic phase demonstrates that we deal with a tetragonal biasing of the titanium motion between off center sites as suggested by Comes, Lambert and Guinier and Chaves et al.. The results show the coexistence of a displacive and a order-disorder component in the phase transition mechanism both in barium titanate and in strontium titanate.

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## Refractive indices, dispersion and thermooptical coefficients of KTP crystal

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The refractive indices, dispersion, and thermooptical coefficients of the KTP ferroelectrical crystal were measured in the region of temperatures of 20-600 C. The least deviation method was used in this case. The refractive indices temperature dependence was determined for four wavelengths:  $\lambda$  464.7 nm, violet,  $\lambda$  546.1 nm, green,  $\lambda$  585.2 nm, yellow,  $\lambda$  632.8 nm, red. It is shown that  $n_o$  and  $n_e$  increases along with the temperature growth. Every curve  $n_{o,e} = f(t)$  can be represented with two crossing lines. The crossing point corresponds to  $\sim 20^\circ$  and is likely to be explained with a phase transition between the incommensurate phases. The  $\Delta$  birefringence value does not change practically with the growth of the temperature and it has the following values: 0.0235, for violet; 0.0219, for green; 0.0216, for yellow; 0.0199, for red. The dispersion curves are presented for the refractive indices of the extraordinary beams  $n_e$  at three different temperatures: 1 -  $20^\circ$ , 2 -  $300^\circ$ , 3 -  $500^\circ$ . It is revealed that the violet line refractive index is more sensible to the temperature change and increases quicker with the temperature growth than the red line refractive index. The thermooptical coefficients are calculated for each wave's length. The thermooptical coefficients changes jumplike at 320 C. The jump of the thermooptical coefficient is much larger for the violet line than for the red one at  $n_e = f(t)$  curve slope change in this case.

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## Oscillations of refractive indices near the phase transitions in (Ba,Na)NbO<sub>3</sub> crystal.

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Temperature measurements of refractive indices for niobate barium-sodium crystal are presented in the work. The least deviation method was employed where the refractive indices are determined according to the angle position of mercury spectrum lines or the laser line. It is shown that there are a number of anomalies on the curves  $n_{o,e} = f(t)$ , where  $n_o$  and  $n_e$  - refractive indices of ordinary and extraordinary rays. Besides the known phase transitions at  $\sim 50^\circ \text{C}$  and  $\sim 80^\circ \text{C}$  there are other peculiarities that could be explain also as the structure phase transitions or as transitions between the incommensurate phases. A special interest is drawn to the space-temporal oscillations of the angle line positions. As a consequence of it the oscillations of refractive indices take place in the temperature regions  $200\text{--}300^\circ \text{C}$  and  $500\text{--}580^\circ \text{C}$ . The oscillations start with the line trembling that turns into the quasiperiodical widening and narrowing of lines relatively their certain middle positions when the temperature of sample increases. The line intensity decreases when widening and vice versa. It worth while mentioning that the lines widen in the direction of the refractive indices increase and the amplitude of such widening increases along the temperature growth. The each line splits into two ones of different intensity with the further increase of temperature. Here the oscillation character changes slightly, the lines join each other and then diverges to the considerable angle distance. When temperature increases the line divergence angle that determine the vibration amplitude increases more and more. The relative intensity of lines also changes. The intensity of the major refractive index line increases along with the minor refractive index line decrease. The angle distance between the lines increases too. The lines oscillate toward one another but they don't merge at this temperature. The minor refractive index line intensity decreases to zero with the temperature increase. The remaining line gets sharp and all the oscillations stop. The further temperature increase leads to the shift in the angle line positions that correspond to the refractive index increase.

The observed oscillations do not seem periodically but they continue appropriately 1-2 seconds. They take place even when heating is stopped. Such phenomena take place in crystals of lithium niobate and lithium tantalite at measurements of temperature dependence of refractive indices too.

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## **Lattice instabilities and dielectric response of nanostructured ferroelectrics**

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We present ab initio results for particular examples of nanostructured ferroelectric perovskite systems, including  $\text{PbTiO}_3/\text{PbZrO}_3$  (001) superlattices, lead titanate and barium titanate thin films and their surfaces, using a pseudopotential implementation of density functional and density functional perturbation theory. We analyze the lattice instabilities of these artificially structured ferroelectrics, which are directly related to their ferroelectric and dielectric properties, showing how they are modified with respect to the bulk constituents. The effects of epitaxial strain, superlattice layering and proximity of a surface on ferroelectric and dielectric properties will also be discussed.

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# Large Scale Simulations of the Relaxor Ferroelectric $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ , with Chemical Order-Disorder and Pb-O Vacancy Pairs: A First Principles Effective Hamiltonian Study

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Experiments indicate that both chemical order-disorder and Pb-vacancies strongly affect the dielectric properties of relaxor ferroelectrics such as  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PSN). Of particular interest are microstructures with 4-10 nm short-range ordered (SRO) domains in a disordered matrix. We use a first-principles based effective Hamiltonian to investigate the effects of ordered microdomains on temperature-dependent properties of  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PSN). Our model is based on Pb-centered polar variables and includes the random local fields at Pb sites which are caused by: 1) B-site chemical disorder; 2) Randomly placed Pb-O vacancy pairs. We create supercells ( $40^3$ -primitive cells) that contain a variety of ordered and partially ordered states: Fully ordered; Random;  $\sim 4$  nm ordered PSN domains in a disordered matrix; a short-range ordered state and some long-range ordered states with various degrees of disorder, that were calculated from first-principles via the cluster expansion (CE) approach. Surprisingly, the CE model predicts a first-order transition for cation order-disorder in PSN. We compute the structure, static dielectric constant, and the polarization inside and outside the microdomains as functions of temperature and compare the results with those for homogeneously disordered PSN.

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## Theoretical Analysis of Domain Engineering Method

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The success of domain engineering process in PMN-PT and PZN-PT single crystals has promoted great interest among materials scientists to understand and utilize this method. People are intrigued to wonder if the method can be applied to other ferroelectric crystals for making better piezoelectric materials or producing non-lead piezoelectric materials with comparable performance to that of lead containing materials. Two of the fundamental questions regarding domain engineering process are: what effective macroscopic symmetry can be produced by this method and what kind of effective properties can be achieved for each fabricated domain pattern when a crystal structure is given. In this talk, we provide a detailed theoretical analysis on these questions based both group theory and elastic compatibility analysis. Statistically, one could obtain many 3-D domain mixtures of existing domains in a crystal structure. These domain patterns form a new level of symmetry that could be either higher or lower than the underlying microscopic crystal symmetry. On the other hand, when we also consider the constraints of elastic compatibility and the requirements of spatial translation symmetry, only very limited domain symmetries can be realized through the application of electric field. Using perovskite structure with crystal structural symmetries of 4mm, 3m and mm2 as examples, we derived all possible effective macroscopic symmetries that can be produced. Property optimization using this domain engineering method will be discussed in depth.

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## First-principles simulations of $\text{K}_2\text{SeO}_4$ dielectrics

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We study from first principles the electronic, structural, dielectric and zone-center dynamical properties of the hexagonal and orthorhombic structures of  $\text{K}_2\text{SeO}_4$ . The two ideally ordered high-T hexagonal phases are a model for many other phases of this compound, obtained by slight distortions of these highly symmetric structures. We determine the lattice and atomic parameters of these phases, and describe their electronic band structure. All the structures present zone-center dynamical instabilities. We compare the zone-center vibrational frequencies with the available experimental data.

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## Automatic generation of lattice Wannier functions

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We present an automatic procedure for generating lattice Wannier functions, which are symmetrized localized displacement patterns analogous to Wannier functions for electron bands. The key step in the construction is finding linear combinations of phonon eigenvectors that (i) span a subspace in which certain important phonons are reproduced exactly, and (ii) smoothly evolve through reciprocal space. This is done using a disentanglement technique that follows closely the theoretical approach developed previously for electrons [1]. This technique maximizes the overlap of this subspace states at neighboring  $\mathbf{q}$  points. The resulting subspace band(s) obey strict symmetry and pattern displacement constraints. The theoretical background will be presented using a simple 1-dimensional triatomic crystal, and preliminary results of the implementation in the ABINIT package will also be shown.

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# First Principles Effective Hamiltonians for Relaxor Ferroelectrics: Distinct Local Variables for each Cation Species

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Relaxor ferroelectrics such as  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN) or  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PSN) often have ferroelectrically “active” species, such as Pb, Nb, or Ta, on both perovskite A and B sites. This suggests that a proper first-principles effective Hamiltonian  $H_{eff}$  for relaxors should have local polar variables on both A and B sites. We develop an  $H_{eff}$  for PSN that includes local polar variables with distinct charges, local potentials, and coupling to strain, for each of the cation species Pb, Sc, and Nb. Inhomogeneous strain and local electric fields due to B-site chemical disorder are also included in  $H_{eff}$ . The form of  $H_{eff}$  allows physical phenomena to be included that can not be incorporated in an  $H_{eff}$  with only one polar variable per unit cell: (1) the effect of size mismatch between Sc and Nb; (2) the effect of cation arrangement on the relative participation of Pb, Sc, and Nb in the soft modes, (3) the possible tendency of Pb and Nb to off-center in different favored sets of directions (*i.e* 001 vs. 111).

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## Towards accurate first-principles simulations of large strain piezoelectric transducer materials

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There are a number of challenges for simulating large strain piezoelectrics such as PMN-PT and PZN-PT that must be surmounted. Firstly, these are complex solid solutions. The substitution of ions of different valence is unlikely to be random.<sup>1</sup> Experiments show the formation of ordered nanodomains that can have a strong impact on properties.<sup>2</sup> How the short- and medium- range order affects ferroelectricity and piezoelectricity in these materials is not clear, but figures in phenomenological models of relaxors.<sup>3</sup> These effects are exceedingly difficult to study in first-principles calculations for small supercells. There are two approaches to extend the length scale that can be studied: effective Hamiltonians and potential models. The former approach has proven very useful so far for PZT type materials, which are simple solid solutions,<sup>4</sup> but have not yet been developed for coupled solid solutions such as PMN-PT. We are exploring the development of shell-model type potentials fitted to first-principles calculations in order to perform large scale molecular dynamics and Monte Carlo simulations. In simple ferroelectric compounds such potentials have been used for studying relatively complex phenomena such as polarization reversal.<sup>5</sup> However in the complex Pb-bearing systems we have run into two problems: fitting potentials accurately to first-principles energies and forces is difficult and there is insufficient accuracy in current density functionals. Even for pure  $\text{PbTiO}_3$ , it is difficult to obtain a potential that has the correct ground state by fitting selected first-principles total energies, forces, and phonon frequencies.<sup>6</sup> This problem is surmountable by varying the potential form and weights, and by including more configurations as input. Unfortunately, for  $\text{PbTiO}_3$  both LDA and GGA are insufficiently accurate. For fixed lattice parameters, LDA and GGA give good piezoelectric<sup>7</sup> and elastic properties. However, the fully optimized structures for  $\text{PbTiO}_3$  are very poor for both LDA and GGA. The WDA has shown great promise for other ferroelectrics,<sup>9</sup> but we also find it insufficiently accurate for  $\text{PbTiO}_3$ . Current progress and improvements will be reviewed.

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## Empirical Modeling of Complex Oxides: The Bond Valence Approach

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We demonstrate how a phenomenological model can be constructed to study complex ferroelectric oxides. This model is derived from a well-known crystal chemistry approach, in which Brown's Rules of Valence are used to determine the configurational energy of the system. Our previous work has shown that this model can be used to explain the atomic interactions in the  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT) solid solution. We shall extend our research to show how this model can be parameterized using a wide array of distorted DFT structures. This parameterization method will be used to test the transferability of the model by observing structural properties of other perovskite oxide ferroelectric systems. Finally, we shall comment on the applicability of this model for finite-temperature and composition-dependent studies.

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## Temporal Effects in Dielectric Properties of Some Antiferroelectric Complex Perovskites

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The antiferroelectrics are very promising materials for various applications as micro actuators and energy storage devices; their fundamental physical properties are still not well understood. The important issue for the soft antiferroelectric (AFE) materials is the relationship between the ferroelectric (FE) and the antiferroelectric ordering as well as the stability of the AFE phase. Two complex perovskite AFE systems were studied; they are  $\text{Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.6}\text{Sn}_{0.3}\text{Ti}_{0.1})\text{O}_3$  (PLZST) in ceramic form and  $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.82}\text{Sn}_{0.12}\text{Ti}_{0.04})_{0.98}\text{O}_3$  (PNZST) thin films. Both materials reveal AFE properties and, according to the phase diagrams, both compositions are close to the morphotropic phase boundary between the FE and AFE regions. Because all published phase diagram data for these two systems are related to room temperature, it is unclear how these systems behave over a wider temperature range. Dielectric and transmission electron microscopy (TEM) studies of the PLZST ceramic confirm the AFE nature of the specimen, but at low temperatures the electrical field application can induce a temporary FE phase with characteristic life-time dependent on temperature. This life-time reaches a value of  $\sim 0.1\text{s}$  at 248K. Further decrease of temperature leads to a much longer time, which exceeds the reasonable laboratory time scale below 210K. We believe that the strongly temperature-dependent kinetics arise from cooperative freezing of the incommensurate AFE order in the presence of a quenched disorder. The PNZST polarization properties are highly dependent on the film thickness and at the lowest limit ( $\sim 170\text{ nm}$ ) the field application in one particular direction can also induce the FE phase with the time of recovery back to the AFE state being a magnitude of several hours. In this case the induction of the FE ordering is very asymmetric with respect to the field direction; it is thickness dependent and the FE phase can be induced if the time of field application is on scale of a second. The application of the field for a much shorter time (e.g. 1ms) does not significantly affect the AFE properties of the films. We suggest that the substrate/film interface could be responsible for this phenomenon.

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## Computer Simulation of Domain Stability and Domain Structures in Ferroelectric Thin Films

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We developed a three-dimensional phase-field model for predicting the domain stability map and the domain structure evolution in an elastically anisotropic single crystal film. It takes into account of the presence of mechanical constraints from a substrate, electrical boundary conditions, as well as the presence of arbitrary spatial distribution of dislocations. A number of examples will be discussed, including the effect of substrate constraint and misfit dislocations on the domain stability map and domain structures in a  $\text{PbTiO}_3$  thin film and the effect of substrate constraint on the PZT phase diagram. It is shown that the mechanical constraint by a substrate can drastically change the relative volume fractions of differently orientated domains and the domain-wall orientations and may even lead to new phases, while dislocations can affect the nucleation, domain wall motion, and the final spatial distribution of domains. It is demonstrated that the assumption of a single-domain ferroelectric state in thermodynamic analysis of domain stabilities in a thin film may result in incorrect domain stability maps.

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## Temperature and Composition Dependence of the Local Environment of Pb Containing Relaxor Systems

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The role of  $\text{Pb}^{2+}$  ion in the relaxor ferroelectric systems, such as PMN, PST and PLZT, are discussed based upon the high-resolution pulsed neutron atomic pair-density function (PDF) obtained with the newly upgraded NPDF spectrometer of the LANSCE, Los Alamos National Lab. The NPDF has the highest  $Q$ -resolution among the powder neutron diffractometers in the US, which translates also to the highest real-space resolution of the PDF. The nature of the Burns temperature was clarified for the first time as the temperature below which the local Pb polarization is dynamically correlated. The local Pb polarization is strongly dynamic even at room temperature, suggesting that lattice dynamics is extremely anharmonic, with a high density of the local phonon modes. The PDF data confirmed that the dielectric relaxation originates mainly in the local Pb motion. The principal origin of the relaxor behavior is the frustration between the local environment of Pb and the average structure, as is illustrated in the composition dependence of the PDF from PZT. In PMN and PST  $\text{Nb}^{5+}$  and  $\text{Sc}^{3+}$  ions play only a minor role, and  $\text{Ta}^{5+}$  shows no polarization.

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## Quantum Chemical Modeling of Polarons and Excitons in $\text{ABO}_3$ Perovskites

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In this paper, we present the state-of-the-art of large scale computer modeling of electron and hole polarons and excitons in advanced  $\text{ABO}_3$  perovskites performed by means of semi-empirical quantum chemical (INDO) method [1-3].

Our calculations confirm existence of the self-trapped electron polarons in  $\text{KNbO}_3$ ,  $\text{KTaO}_3$ ,  $\text{BaTiO}_3$ , and  $\text{PbTiO}_3$  crystals. The self-trapped electron is mostly localized on B-type ion due to a combination of breathing and Jahn-Teller modes of nearest 6 O ion displacements. The relevant lattice relaxation energies are typically 0.2 – 0.3 eV, whereas the optical absorption energies 0.7 – 0.8 eV, respectively. The optical absorption energies for the electron polaron bound to Mg impurity in  $\text{KNbO}_3$  (0.88 eV) and hole polaron bound to K vacancy ( $\approx 1$  eV) are also in good agreement with the relevant experimental data [4].

Our INDO calculations demonstrate that creation of charge-transfer vibronic exciton (CTVE) in these crystals is accompanied by a strong lattice distortion. We suggested interpretation of the so-called green luminescence in these crystals (with a peak around 2.2 – 2.3 eV) as a result of the radiative recombination of nearest electron and hole polarons. The relevant experimental data are discussed [5].

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## Quantum Chemical Modeling of Phase Transitions in Perovskite Solid Solutions

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The large-scale modeling of the atomic and electronic structure of  $\text{KNb}_x\text{Ta}_{1-x}\text{O}_3$  (KTN) perovskite solid solutions is performed using the Intermediate Neglect of the Differential Overlap (INDO) method based on the Hartree-Fock formalism. It is found that periodic Nb impurities in  $\text{KTaO}_3$  reveal coherent off-center displacements beginning with the smallest calculated concentrations  $x = 0.125$ . The calculated magnitude of [111] Nb-off centre displacement is 0.27 a.u., which is close to the XAFS observation at 70 K and  $x = 0.09$ . In contrast, Ta impurities in  $\text{KNbO}_3$  remain on-center, due to higher ionicity of Ta as compared to Nb. Using the calculated energy gain caused by the off-center displacements of Nb atoms, we construct the non-empirical Ginzburg-Landau-Devonshire functional with concentration-dependent coefficients and use it for several Nb concentrations in KTN. This allows us to predict the change from paraelectric phase to ferroelectric displacive phase in KTN at  $x_{cr} = 0.025$ , which is slightly higher than experimental value.

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## First-principles calculations of piezoelectric response under finite electric fields

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A practical and rather simple approach is implemented to calculate from first principles the piezoelectric responses of ferroelectric materials under finite and static electric fields. The approach is based on simultaneous minimization of free energy and total force. By avoiding linear perturbation theory, the approach is easy to implement in first-principles codes. We applied this method to calculate the piezoelectric responses in tetragonal  $\text{PbTiO}_3$ . The computed piezoelectric coefficient and susceptibility are in good agreement with experiments. If time permits, we will also present studies on  $\text{BaTiO}_3$  ferroelectric quantum dots.

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## Morphotropic Boundaries in High Temperature Ferroelectrics

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Because of a recent discovery of intermediate phases at the morphotropic boundaries in PZT, PMN, and PZN materials, there is a renewed interest in understanding basic physics of morphotropic boundaries in ferroelectric materials. Presence of intermediate phases is consistent with highly spherical energy function. The isotropy of energy function leads to anisotropic piezoelectric and dielectric tensor properties for compositions at the MPB with the anomalously large constants originating from easy rotation of polarization. A similar anisotropy of properties can be obtained either by temperature-induced phase transitions in BaTiO<sub>3</sub> or by changing composition of lead containing ferroelectrics. Thus intermediate phases are a byproduct of degeneracy of the energy function and are not essential for superior properties at the MPB.

Recent work on Bi(Me'Me'')O<sub>3</sub> - PBTiO<sub>3</sub> systems indicates that it is possible to combine high transition temperature with excellent piezoelectric properties. Similar to PZT ceramics, best properties were obtained in the vicinity of the MPB. This work emphasized: 1) the importance of tolerance factor in predicting the MPB transition temperature in lead containing ceramics, and 2) relevance of tilted transitions in the vicinity of the MPB on the magnitude of piezoelectric coefficients. In particular, BiScO<sub>3</sub> - PbTiO<sub>3</sub> system has phase diagram similar to PZT and shows superior piezoelectric properties.

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## PMN-10%PT is not Rhombohedral

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The currently accepted phase diagram of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  doped with  $\text{PbTiO}_3$  (PMN- $x$ PT) exhibits a rhombohedral ground state for low  $\text{PbTiO}_3$  concentrations<sup>1</sup> with the exception of pure PMN ( $x = 0$ ), which retains an average cubic structure at low temperature.<sup>2</sup> X-ray measurements by Dkhil *et al.* show clear evidence of a rhombohedral splitting of the (222) peak for PMN-10%PT at 80 K, as well as a peak in the diffuse scattering intensity at  $T_c = 285$  K.<sup>1</sup> However, recent neutron scattering measurements of the same compound at (111) with comparable  $q$ -resolution show a single resolution-limited peak at 100 K, and thus no rhombohedral distortion. Moreover, the diffuse scattering increases monotonically with decreasing temperature. These results are examined in the context of the new phase X, which has a nearly average cubic structure, observed in PZN by G. Xu *et al.* using high energy x-rays.<sup>2</sup> We propose a new phase diagram for both PZN- $x$ PT and PMN- $x$ PT that consists of cubic, phase X, and monoclinic and tetragonal phases at higher  $x$ . The observed rhombohedral phase exists only in the “skin” of the crystal, of order a few microns thick, and thus dominates the x-ray scattering. Establishment of the rhombohedral phase in the crystal bulk can be achieved by application of an applied electric field along the [111] direction.

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**Effects of atomic short range order on the properties of  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  alloy  
near its morphotropic phase boundary**

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The effects of *atomic short range order*, clustering and anti-clustering, on the properties of  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  alloy near its morphotropic phase boundary (MPB) are studied by combining first-principles-based methods and annealing techniques. We find that atomic short-range order drastically affects the compositional range delimiting this MPB. In particular, the clustering of like atoms leads to an expansion of this boundary, while the anti-clustering of like atoms leads to a contraction of this compositional region. In other words, atomic short-range order can induce phase transitions inside the MPB. Microscopic effects responsible for these anomalous properties will be presented and discussed.

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# Thickness-dependence of the ferroelectric properties in perovskite ultrathin film

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ABO<sub>3</sub> ferroelectric perovskites are promising candidate materials for Non-volatile Ferroelectric Random Access Memories (FeRAM). Industry's demand for ultrahigh density information storage forces the reduction of the cell-sizes and thicknesses of the ferroelectric films while some size effects should be expected on the ferroelectricity of the system. Previous first-principles based effective hamiltonian calculations <sup>1</sup> and full first-principles simulations <sup>2</sup> predicted ferroelectric ground states for ABO<sub>3</sub> thin films under zero field boundary conditions. However, the role played by real metallic electrodes on the structure and polarization of the system was missing in the previous approaches. We report density-functional first-principles calculations <sup>3</sup> on a realistic SrRuO<sub>3</sub>/BaTiO<sub>3</sub>/SrRuO<sub>3</sub> ferroelectric capacitor under short-circuit boundary conditions. A critical thickness for ferroelectricity is identified and valued at 24 Å (six unit cells of BaTiO<sub>3</sub>). A depolarizing electrostatic field, caused by dipoles at the metal/ferroelectric interfaces is responsible for the disappearance of the ferroelectricity. Above the critical thickness, we recover a polarized ground-state, although with a reduced spontaneous polarization with respect to the bulk, in good agreement with experimental results <sup>4</sup>. A model, based only on the electrostatic of the system, is proposed to explain the evolution of the ferroelectric properties with the film thickness. Our results suggest a lower limit for useful thicknesses of these materials in electronic devices.

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## Ab Initio studies of silver based ferroelectrics

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Using DFT calculations, we investigate the local structure and the distortion patterns of the perovskite AgNbO<sub>3</sub>. Our calculations show that silver atoms can off-center by about 0.5 Å, forming short covalent bonds similar to the short Pb-O bonds in Pb-based ferroelectrics. We also investigate several solid solutions based on AgNbO<sub>3</sub> and show that they may possess good piezoelectric properties.

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## Local Structure in Lead based ferroelectrics by DFT calculations

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We use DFT calculations on 40- and 60-atom supercells to study the local structure of a series of Pb based ferroelectrics including the relaxors PMN and PZN. We show that transition metal B-cations are capable of ferroelectric distortion, while the simple metal Mg is not. This may account for the differences between PZN and PMN in T<sub>c</sub> and in the location of the morphotropic phase boundary when alloyed with lead titanate. The role of under- and overbonded oxygens in controlling the local polarization direction is discussed.

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# First Principles Investigation of Novel Ferroelectric Perovskite Alloys Based on A-site Substitution

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We report first principles studies of the lattice instabilities of as yet unsynthesized perovskites based on alloying PbTiO<sub>3</sub> with CdTiO<sub>3</sub> and on alloys in the (Th,Pb,Ba,Bi,Y)ScO<sub>3</sub> system. These systems are characterized by strong structural instabilities of the cubic perovskite lattice and A-site driven ferroelectricity. Tetragonal ferroelectric structures in these systems are found to show rather large values of the  $c/a$  ratio, which when present near a morphotropic phase boundary are associated with large piezoelectric actuation. The relationship between rotational and ferroelectric instabilities is discussed as are the conditions for obtaining a morphotropic phase boundary.

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# First-principles study of oxygen vacancy pinning of domain walls in $\text{PbTiO}_3$

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Certain models of fatigue (i.e., the degradation of the saturation polarization with repeated switching) involve pinning of ferroelectric domain walls by point defects. However, the microscopic interactions between domain walls and point defects remain poorly understood. As a first step in this direction, we have investigated the interaction of oxygen vacancies and  $180^\circ$  domain walls in tetragonal  $\text{PbTiO}_3$  using density-functional theory. Our calculations indicate that the vacancies do have a lower formation energy in the domain wall than in the bulk, thereby confirming the tendency of these defects to migrate to, and pin, the domain walls. The pinning energies are reported for each of the three possible orientations of the original Ti–O–Ti bonds, and attempts to model the results with simple continuum models are discussed.

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## Ab initio calculations of the polar surface structure for SrTiO<sub>3</sub> perovskite

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As continuation of our recent studies [1-3], in this paper we present and discuss results of ab initio modeling of the atomic and electronic structure of SrTiO<sub>3</sub> polar (110) surface. These calculations are performed using Hartree-Fock method with electron correlation corrections and HF-DFT B3LYP hybrid method. as implemented into CRYSTAL-98 computer code.

The obtained surface relaxation and rumpling are in a good agreement with classical shell model calculations [4]. We discuss two different models for the O-terminated stable surface without dipole moment perpendicular to the surface and analyze chemical bonding covalency effects near the surface.

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## Micro-Brillouin investigations on relaxor ferroelectrics

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Brillouin scattering probes the inelastically scattered light from acoustic excitations. This information directly reveals the sound velocity along a certain direction in the material. The sound velocity in polar ferroelectrics can be used to calculate elastic constants  $c_{ijkl}$  and piezoelectric coupling constants  $e_{ijk}$ . While the temperature and pressure dependence of the elastic constants reveals essential information about the phase transitions in ferroelectrics, detailed knowledge on the piezoelectric constants provides important information for practical applications. Micro Brillouin measurements are especially interesting as a probe because of the possibility to investigate small regions down to 20  $\mu\text{m}$ , so that single domain measurements can be realized. In contrast to common ultrasonic measurements we can therefore probe single crystal properties and obtain information on all  $c_{ijkl}$  and  $e_{ijk}$ .

Especially the relaxor ferroelectrics in the solid solution of  $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$  and  $\text{PbTiO}_3$  (PZN-PT) and  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  and  $\text{PbTiO}_3$  (PMN-PT) are of practical interest and still pose a challenge understanding the extreme electro-mechanical properties on a fundamental level. We started our investigation with the end member lead titanate (PT) where large discrepancies were reported for the determination of especially the piezoelectric constants among different Brillouin investigations<sup>1</sup>. Preliminary results from our new investigations show two new effects that explain the observed uncertainties in prior investigations and pave the way for reliable determination of the piezoelectric constants in micro samples: We observed an additional signal that can be explained by pure elastic contribution without piezoelectric coupling. This signal most likely originates in domain walls between two  $180^\circ$  domains. In these regions the spontaneous polarization is zero and can therefore not contribute to the sound velocity. In our spectra we can clearly observe a significant splitting of the longitudinal and one transversal mode. The splitting can be attributed to piezoelectric coupling. A second effect is related to the occurrence of a central peak in light scattering experiments of ferroelectrics<sup>2</sup>. The central peak is a relic of the cubic-to-tetragonal phase transition at 768 K and can be described as entropy fluctuations related to the soft-mode. We found a pronounced coupling between the central peak and the acoustic wave which introduces a strong asymmetric line shape in the spectra. The coupling is strongly dependent on the direction and will be discussed in its effect on the ferroelectric properties in general.

Further investigations on PZN-PT and PMN-PT are especially interesting with respect to the extremely high piezoelectric coupling in these relaxor type materials. Measurements are underway and in addition to the above mentioned techniques we will also use transparent electrodes to analyse the detailed effect of domain formation *in situ* and to additionally measure the electric field dependence of the acoustic properties. The use of transparent electrodes in combination with Brillouin scattering has not been reported yet and will provide an additional possibility to distinguish between purely elastic and piezoelectric contributions. Results from these investigations are very promising and are especially suited to resolve the detailed and complicated interplay between the pure elastic and the piezoelectric contributions. From these measurements a more complete picture of the special nature of the morphotropic phase boundary in relaxor type materials can be drawn and the elastic and piezoelectric constants will be characterized.

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## What do we learn from diffuse scattering in cubic relaxor ferroelectrics

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Recently, important progress was achieved in describing diffuse scattering in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{1/3})\text{O}_3$  and  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{1/3})\text{O}_3$  pure and  $\text{PbTiO}_3$  doped relaxor ferroelectric crystals (PMN:PT, PZN:PT), namely due to the extensive X-ray and neutron scattering studies[1-7]. In this contribution we will try to overview the available experiments and models describing diffuse scattering in these materials[1-8], and comment on possible interpretations on the basis of our own recent cold neutron scattering investigation of PZN:8PT single crystal.

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# First-principles study of $(1-x)\text{BiScO}_3\text{-}x\text{PbTiO}_3$ piezoelectric alloys

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Recent work [1] has focused attention on  $(1-x)\text{BiScO}_3\text{-}x\text{PbTiO}_3$  (BS-PT) as an interesting candidate material in the family of piezoelectric perovskite alloys, of which the best known is  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT). The appeal of BS-PT is twofold: (i) it displays a morphotropic phase boundary (MPB) with enhanced piezoelectric response in its vicinity, and (ii) the Curie temperature at the MPB is substantially higher than that of PZT, widening the potential temperature range of stable device operation. We have performed a first-principles study of BS-PT aimed at understanding its promising properties. Our results indicate that (i) BS-PT displays very large structural distortions and polarizations at the MPB (we obtain  $c/a$  lays between 1.05 and 1.08, and  $P_{\text{tet}} \approx 1.1 \text{ C/m}^2$ ); (ii) the ferroelectric properties of BS-PT are mainly related to the onset of hybridization between Bi/Pb-6*p* and O-2*p* states, a mechanism that is enhanced upon substitution of Pb by Bi; and (iii) the piezoelectric response of BS-PT at the MPB is comparable to that of PZT. While our results are generally consistent with experiment, they also suggest that certain intrinsic materials properties may be even better than has been indicated by experiments to date.

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## Local Structure – Properties Relations in the $(1-x)\text{Pb}(\text{Sc}_{2/3}\text{W}_{1/3})\text{O}_3 - (x)\text{Pb}(\text{Ti/Zr})\text{O}_3$ Relaxors

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The solid solutions of  $(1-x)\text{Pb}(\text{Sc}_{2/3}\text{W}_{1/3})\text{O}_3 - (x)\text{PbTiO}_3$  (PSW–PT) and  $(1-x)\text{Pb}(\text{Sc}_{2/3}\text{W}_{1/3})\text{O}_3 - (x)\text{PbZrO}_3$  (PSW–PZ) show relaxor response with remarkably different behavior. For PZ the transition (maximum) temperature ( $T_{\epsilon, \max}$ ) grows with  $x$ , however it is decreased for additions of Ti up to  $x \approx 0.25$ , in spite of PT having much higher Curie temperature (763K) than PZ (503K). To understand this behavior, the effect of PT and PZ on the structure and ordering of PSW was studied using synchrotron x-rays and neutron diffraction. Rietveld refinement was carried out to determine the average long-range crystallographic structure and pair distribution function (PDF) analysis to probe the local displacements of the atoms. For  $x < 0.25$  the B-cations form a 1:1 ordered doubled perovskite structure (space group  $Fm\bar{3}m$ ). The B-occupancies determined by Rietveld method gave an excellent agreement with a “random site model”, where completely ordered structure consists of one B-sublattice occupied by Sc and the other by a random mixture of the remaining cations. The B-site order is reduced by the incorporation of Zr, but highly stabilized by Ti with the degree of order in excess of 95% for  $x \leq 0.25$ . Refined temperature factors for Pb and O were unrealistically large and indicated local distortions from the average structure. Local atomic structure has been probed by analyzing PDF from the neutron diffraction data, which were collected at temperatures above (290K) and below (20K) the paraelectric transition. The experimental PDF curves were considerably different from the values expected for an ideal perovskite structure and their peaks sharpened at low temperature. This confirmed that on the local scale the Pb and O atoms are significantly displaced from their average lattice positions and their displacements get less correlated at higher temperatures. The experimental PDF curves were simulated by several models of simple Pb and O displacements, using the steepest descent and Monte Carlo methods. Distortions of the local structure in  $\text{Pb}(\text{Sc}_{2/3}\text{W}_{1/3})\text{O}_3$  and  $\text{Pb}(\text{Sc}_{1/2}\text{W}_{1/4}\text{Ti}_{1/4})\text{O}_3$  ( $x = 0.25$ ) were also modeled by density functional theory calculations. The relationships between the local displacements, composition, cation order and the dielectric properties will be discussed.

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## Domain states in uniaxial relaxors and quantum ferroelectrics

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Non-Debye relaxation processes are observed in the random-field induced ferroelectric domain state of the uniaxial solid solution strontium barium niobate (SBN). Because of its inherent quenched charge disorder this system is probably the most perfect materialization of the three-dimensional ferroic random-field Ising model (*RFIM*). It shows modified critical and drastically slowed-down dynamic behavior. While polydispersive relaxation of pinned domain wall segments characterizes the *rf* regime, creep of the domain walls gives rise to Curie–von Schweidler (*CvS*) type very low-frequency (*vlf*) dispersion of the complex susceptibility. The *CvS* exponent is shown to vary drastically when reducing the domain wall density. A dynamic phase transition, where the order parameter  $Q = (\omega/2\pi) \oint P dt$  changes from  $Q = 0$  (*rf*) to  $Q \neq 0$  (*vlf*), separates both dispersion regimes. Similar processes are observed in the quantum ferroelectric  $\text{SrTi}^{18}\text{O}_3$ . Its domain state is attributed to pinning by quenched defects, which are produced during the exchange of the oxygen isotopes,  $^{16}\text{O} \rightarrow ^{18}\text{O}$ .

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# Finite-Temperature Properties of PZT Superlattices Near the Morphotropic Phase Boundary From First Principles

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Finite-temperature properties of  $[\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3]_n/[\text{Pb}(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3]_n$  superlattice structures are simulated using ab-initio-based approaches. More precisely, we explore superlattices with variable periodicity  $n$ , and with  $x$  and  $y$  compositions located *across* the morphotropic phase boundary of disordered PZT. Furthermore, the average  $\frac{x+y}{2}$  composition lies *inside* this boundary and thus yields a monoclinic  $M_A$  ground state for the disordered PZT bulk. Interestingly, our results show that at low temperature, our studied superlattices adopt a global minimum that is ferroelectric and of unexpected *triclinic* symmetry, and also exhibit a local minimum of monoclinic  $M_A$  symmetry. Furthermore, some electromechanical responses are enhanced in the global minimum with respect to the local minimum because of the resulting lowering of symmetry. The energetic difference between the global and local minima increases when increasing the difference in composition  $|x - y|$  and/or the periodicity  $n$ . We also obtain detailed information about the role of different microscopic interactions on the physical properties of these superlattices. In particular, the inhomogeneous strain fields, resulting from the size mismatch between Ti and Zn atoms, is found to play a noticeable role on these anomalous properties.

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# Quantum Monte Carlo method using phase-free random walks with Slater determinants

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In order to do accurate calculations to predict materials properties across length scales, it is critical to have robust and reliable calculations at the most fundamental level. Often the desired effects of the materials being designed originate from electron interaction and correlation effects, and small errors in treating such effects will result in crucial and qualitative differences in the properties. In perovskite ferroelectric materials, for example, properties such as phonons, polarizations and crystal structure are very sensitive to the volume. The local density approximation (LDA) generally underestimates the equilibrium volume while generalized gradient approximations (GGA) tend to overestimate them. The weighted density approximation (WDA) may improve agreement in some cases, and this approach is under active investigation.

Quantum Monte Carlo (QMC) methods allow essentially exact calculations of ground-state and finite-temperature equilibrium properties of interacting many electron systems, with algorithmic complexity scaling in principle as a power law with system size [compared to exponential scaling with direct approaches such as the configuration interaction (CI) method]. A principle difficulty has been the complexity of the required trial wave functions in the standard methodology. The trial wave function  $|\Psi_T\rangle$  is used for three purposes in the standard diffusion Monte Carlo (DMC) methodology: (i) to provide the nodes for the fixed-node approximation, which is necessary to control the well-known fermion sign problem, (ii) to calculate the non-local part of the pseudopotential in the locality approximation, which has been employed by most DMC calculations to implement non-local pseudopotentials, and (iii) to do importance sampling to control the Monte Carlo variance. Obtaining a good enough  $|\Psi_T\rangle$  is instrumental to any successful DMC calculations, and often constitutes the bulk of the effort.

We have developed a quantum Monte Carlo method [1] using Hubbard-Stratonovich auxiliary fields. Aimed at treating electron correlations in real materials, this is a many-body method that shares much of the machinery of standard density functional methods. The method projects out the ground state by random walks in the space of Slater determinants. An approximate approach is formulated to control the phase problem with a trial wave function. The formalism allows the use of any set of one-particle basis functions. For periodic systems it allows arbitrary  $k$ -point sampling with twisted boundary conditions. Using a plane-wave basis and non-local pseudopotentials, we apply the method to Si and P atoms and dimers, and to bulk Si with a 54 atom (216 electrons) supercell. Single Slater determinant wave functions from density functional theory calculations were used as the trial wave function with no additional optimization. The calculated dissociation energy of the dimer molecules and the cohesive energy of bulk Si are in excellent agreement with experiment and are comparable to the best existing theoretical results.

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**Phonon Anomaly of the Relaxor Ferroelectric  
(1- $x$ )Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>- $x$ PbTiO<sub>3</sub> by Neutron Inelastic Scattering**

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Neutron inelastic scattering measurements have been performed on single crystal samples of the relaxor ferroelectric (1- $x$ )Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>- $x$ PbTiO<sub>3</sub> (PZN- $x$ PT) with  $x = 0, 4.5$ , and  $9\%$  as a function of temperature. The experiments have revealed broadening of the transverse acoustic (TA) phonon mode at intermediate  $q$  values and the appearance of a central peak, both due to the formation of the polar nanoregions upon cooling. At the condensation temperature of the polar regions, the central peak intensity goes through a maximum, below which they reorient as single units (giant dipoles). Their reorientational motion is detected indirectly through coupling to the TA mode and directly through the central peak. With increasing PT, the lattice becomes more rigid and the polar regions are less able to reorient, resulting in the lower damping of the TA phonon.

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## Giant Electrostriction in Ferroelectric Polymer Based Composites

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We propose a ferroelectric polymeric composite concept with dramatically-enhanced effective electrostriction, strain energy density, and electromechanical coupling factor, where high-dielectric-constant ceramics are embedded in ferroelectric polymers to increase the electrostrictive strain. Using a nonlinear micromechanics model we developed, we were able to predict the macroscopic behaviors of ferroelectric polymer based composites in terms of the properties of the constituent phases and the micro-geometry, and were able to demonstrate the importance of the size effect, the dielectric constant and the microstructure on the effective electrostriction of the composites. The giant electrostriction recently demonstrated in an all-organic composite at Penn State University has also been explained.

This work was supported by the University of Nebraska-Lincoln.

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## Point Defects and Physical Properties of Ferroelectrics: Lithium Niobate

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Fast development of opto-, acoustoelectronics and photonics requires for new materials with the improved characteristics. Sometimes the requested quality or parameter can be successfully achieved from the well-known, commonly used material with respective changes to its defect system. The results supporting this approach have been recently obtained for ferroelectric Lithium Niobate ( $\text{LiNbO}_3$ , LN). The analysis of intrinsic (non-stoichiometric) and extrinsic (impurity) defects in LN crystals and strong dependence of crystal properties on defects concentration (up to two orders of magnitude) forms the topic of the talk. It is mainly based on the results of our experimental and theoretical studies combined with the available literature data. The spectra of magnetic resonances (EPR, NMR, ENDOR), HREM, optical and X-ray structural analyses data have been analyzed for LN crystals with different compositions, diverse modifiers and various probe impurities. The results show clearly that crystals with the extremely low concentration of intrinsic defects offer extraordinary informative opportunities for fundamental physics. The strong interrelation of the subsystems of intrinsic and extrinsic defects becomes especially apparent when concentrations of both defect classes are comparable. Finally, the stress will be laid on the conclusion, that materials having tendency to grow in non-stoichiometric composition offer especially rich opportunities for crystal engineering, since both intrinsic and extrinsic defect subsystems can be used for deliberate tailoring material properties. The ideas developed in this work have a general character; therefore they should also be valid for other non-stoichiometric oxide ferroelectrics.

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## Calculated Electric Field Gradients in Tetragonal and Monoclinic PZT

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High magnetic field MAS NMR measurements have recently shown great promise as a microscopic probe of structure in complex perovskite ( $\text{ABO}_3$ ) PMN type solid solutions [1], by their ability to resolve electric field gradient (EFG) splittings. It is thus of considerable interest to be able to calculate EFG's in these materials. Here we present local-density-functional LAPW EFG calculations for PZT(50/50) focussing on trends in EFG's in the tetragonal and monoclinic phases. Pb exhibits a 10-fold increase in monoclinic EFG's, but unfortunately Pb has no nuclear quadrupole moment. O EFG's are similar to those in tetragonal  $\text{PbTiO}_3$  (PT) and show small variations in the PZT phases. Ti EFG's are much larger than in PT and show slightly larger variations, while Zr EFG's increase by about 50

[1] G. Hoatson et al., PRB, in press.

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## Car-Parrinello Molecular Dynamics with Wannier Functions

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We present a formulation of Car-Parrinello (CP) molecular dynamics in which the electronic orbitals, following adiabatically the nuclear dynamics, are represented by maximally localized Wannier functions [Marzari and Vanderbilt, Phys. Rev. B **56**, 12847 (1997)]. This scheme requires only a modest computational overhead compared to standard formulations based on delocalized electronic orbitals. The Wannier-based approach allows us to simulate bulk dielectric materials in presence of a uniform external electric field. We demonstrate the viability of the scheme with extensive simulations on a liquid water sample containing 64 molecules in a periodically repeated box. Preliminary results of simulations on liquid water in presence of an external uniform static electric field will be presented.

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# Impact of Antiphase Domain Boundaries on the Dielectric Response of $Ba_xSr_{1-x}TiO_3$ Thin Films

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Epitaxial  $Ba_xSr_{1-x}TiO_3$  (BST) films grown on MgO substrates have a high density of anti-phase domain boundaries (ADB's). These defects are believed to be one of the primary causes for the lowering of the dielectric constant of the films compared to bulk. We investigate the impact of ADBs on the dielectric constants of BST films combining first-principles pseudopotential plane-wave density functional calculations with a Landau-Ginsburg approach. We found that the ADBs act to lower the in-plane dielectric constant in several different ways. First, the dielectric response perpendicular to the ADBs is reduced due to the breaking of the infinite Ti-O chains normal to the boundaries. To show this we have calculated the dielectric properties of  $SrTiO_3$  with an ordered array of ADBs. Comparing with the dielectric response of ideal  $SrTiO_3$ , we found that the dielectric response perpendicular to the ADBs is reduced by a factor of 5-8. Second, within a Landau-Ginzburg analysis we find that the ADBs parallel to the electric field also lead to a significant reduction in the dielectric constant, as their effective width is given by the coherence length. Finally, the dielectric constant may be even further reduced by a segregation effect near the ADBs. Using ordered supercells and the virtual crystal approximation we discovered that in BST with Ba/Sr-rich APB's, enhancement of the relative Ba/Sr concentration near the boundaries is energetically favorable, raising the Sr concentration in the remainder of the film. This should stabilize the paraelectric state and, consequently, lower the net dielectric constant.

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## First-principles study of multiferroism in BiFeO<sub>3</sub>

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The ground state of BiFeO<sub>3</sub> is known to exhibit both ferroelectricity and ferromagnetism (i.e., multiferroism), an intrinsic multifunctionality that would ostensibly make it a strong candidate for nanoscale electronics applications. Both its spontaneous polarization ( $\sim 6\mu\text{C}/\text{cm}^2$ ) and saturation magnetization ( $\sim 0.1\mu\text{B}/\text{formula unit}$ ), however, are disappointingly low when compared to many standard ferroelectrics or ferromagnets. The empirically-small polarization is particularly perplexing as it is at odds with x-ray measurements, which reveal a rhombohedral  $R3c$  arrangement and unusually large displacements from the cubic perovskite structure ( $Pm\bar{3}m$ ). To gain atomic-scale insight into the origin of its macroscopic behavior, we compute the structure, polarization, dielectric, and magnetic properties of BiFeO<sub>3</sub> using first-principles density-functional theory within the local spin-density approximation (LSDA). Our computed ground state structure, relaxed within  $R3c$  symmetry, is in excellent agreement with available experimental results; notably, we find a large off-centering of Bi cations relative to tilted FeO<sub>6</sub> octahedra. The Berry-phase polarization of the  $R3c$  phase, however, is found to be an order of magnitude larger than previously reported for bulk crystals, in striking agreement with a recent experiment on epitaxially-grown thin films [1] and in line with the observed large displacements. The calculated antiferromagnetic ground state is consistent with the observed “weak” ferromagnetism, i.e., that arising from a long-range ( $\sim 60$  nm) spiral spin structure superimposed on an otherwise antiferromagnetic order. The discrepancy between the behavior of BiFeO<sub>3</sub> in thin film and bulk geometries, and the implications for enhancing its ferroelectric and ferromagnetic properties, are thoroughly discussed.

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## Nanoscale effects in PZT Thin Films by Piezo-response studies

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Ferroelectric capacitor dimensions for 1 Gbit NVFRAM must have sub-micron lateral size and thickness. In a ferroelectric capacitor, electrodes and substrate impose various kinds of constraints on the ferroelectric layer, among which the mechanical constraint is of critical importance. The interplay between the mechanical properties of the substrate/electrodes and the ferroelectric layer can lead to dramatically decreased dielectric and piezoelectric coefficients. We present in this talk a detailed investigation on the effects of vertical size scaling. We chose 4 different geometrical configurations (LSCO/STO, LSCO/STO/Si, SRO/STO and SRO/STO/Si), and 3 different orientations-(001), (110), (111). These configurations allow us to compare properties on various prototypical platforms where physical parameters such as lattice mismatch, thermal mismatch and domain configurations can be systematically altered. The PZT layer is deposited on these substrates using various techniques including MOCVD and high pressure sputtering. Comprehensive ferroelectric and piezoelectric measurements were performed for PZT thickness varying from 20 nm to  $\sim 1\mu\text{m}$ . Although the capacitors exhibit ferroelectric properties for thickness down to at least 20 nm, a drastic decrease in the piezoelectric constant is observed for sub-100nm thick films. We will present the results of our investigations on possible causes for this degradation.

Secondly, while (001) oriented films exhibit the traditional butterfly loop (a decrease in  $d_{33}$  with increasing electrical field after it reaches its maximum value), a significantly different response is observed in (111) and (110) oriented films. By a Landau-Ginzburg-Devonshire type phenomenological explanation, we show that the non-linear electric field dependence of dielectric susceptibility is the origin of this phenomenon. Further calculation shows the dielectric susceptibility of a thin film is a function of electric field ( $E$ ), elastic compliance ( $S$ ), dielectric stiffness ( $a$ ) and electrostrictive constants ( $Q$ ) under high field. Using a modified LGD approach we will present a model that explicates the electric field- $d_{33}$  dependence for various film-substrate epitaxial relationships.

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## First Principles Calculations of Lattice Dynamics in Some $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Supercells

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Lattice dynamics and Born effective charges were calculated for several ordered supercells of  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ , using density functional theory. In each supercell, ferroelectric, antiferroelectric, and octahedral tilting instabilities occur. Competition between the various instabilities makes it difficult to determine ground states, but candidate ground states are identified for each ordered structure. Lattice dynamics for the candidate ground state structures were also calculated, as were infrared reflectivity spectra, which are compared to experimental data.

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## Diffusive phase transitions in ferroelectrics and antiferroelectrics

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We discuss new experimental data on antiferroelectrics exhibiting diffusive phase transitions like sodium niobate with an admixture of Gd, and an iron- containing ferroelectric ternary perovskite showing the same property. In both examples a Vogel-Fulcher law is true, there is a frequency dispersion at the dielectric permittivity peak position although in the ferroelectric relaxors it is much more pronounced. One of the main differences is a comparatively low dielectric permittivity in antiferroelectric relaxors, and the position of the extrapolated Curie-Weiss temperature with respect to the dielectric permittivity peak temperature in ferroelectric relaxors is at higher temperatures, but in antiferroelectrics it is at lower temperatures.

In both cases we explain the diffuseness of the dielectric permittivity peak by the interaction of the corresponding order parameter with quenched fields produced by frozen fluctuations of the order parameter. Examples of scalar and vector order parameters will be considered. The expression obtained allows one to fit the Curie-Weiss tail from the high temperature side simultaneously with the diffusive (quadratic with temperature) region as well as with a Curie-Weiss tail from the low temperature side.

We have a special concern in the ferroelectric relaxor state and consider it from a point of a microscopic model which includes several ferroelectric slabs interlaid with dielectric layers. We show that such a system gets broken into nanodomains with zero total polarization due to the compensation of the depolarization field and elastic misfits. We assumed that the relaxor state has its own order parameter and it corresponds to a wave of polarization followed by shear strain. We have performed a computation of the neutron scattering intensities for such nanodomains and obtained a qualitative agreement with experiment.

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# CATION ORDERING IN SINGLE CRYSTALS OF 1:1 AND 1:2 COMPLEX PEROVSKITES SOLID SOLUTIONS

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Solid solution single crystals of some ternary  $\text{PbB}'_n\text{B}''_m\text{O}_3$  perovskites displaying colossal dielectric, piezoelectric, electrostrictive, electrooptic responses are promising materials for various applications. The dramatic effect of ordering degree  $S$  on ferroelectric Curie temperature  $T_c$  in compositionally orderable 1:1 ternary perovskites (e.g.  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PSN)) leads to rather complicated character of their solid solutions phase diagrams. Ordering effects have been reported for several solid solutions of 1:2 (e.g.  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN)) ternary perovskites as well. Usual  $T-x$  phase diagrams are insufficient for complete characterization of compositionally orderable solid solutions without taking account of  $T-S$  sections of the general  $T-x-S$  phase diagram.

In the present study  $(1-x)\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3 - (x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  (PSN-PST) and  $(1-y)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - (y)\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PMN-PSN) solid solution crystals have been grown by the flux method in a whole concentration range. X-ray supercell reflections due to B-cation ordering were observed for as-grown crystals from the  $0.2 \leq x \leq 1$  and  $0.1 \leq y \leq 0.65$  compositional ranges.

The temperature  $T_t$  of the compositional order-disorder phase transition for PSN-PST was found to be an approximately linear function of composition. For  $(1-y)\text{PMN}-y\text{PSN}$  system  $T_t(y)$  was reported to be a parabolic function of  $y$  [1]. Basing on the Bragg-Williams approximation in the alloy theory we explicitly obtained the analytical expression for the temperature  $T_t$  of the compositional order-disorder phase transition in the compositionally orderable solid solution giving either of these dependences.

The results obtained are consistent with the model of ordering process during the growth of ternary perovskite crystals, proposed earlier for  $\text{PbSc}_{0.5}\text{Nb}_{0.5}\text{O}_3$  and  $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$  [2]. According to this model during the crystal growth the disordered structure is formed first even when the crystallization temperature is much lower than  $T_t$  and the disordered phase is non-equilibrium. The ordering then starts via a diffusion-type mechanism, its rate depending greatly on the relation between the crystallization temperature and  $T_t$ . According to this model, a parabolic shape of the  $T_t(x)$  dependence for  $(1-y)\text{PMN}-y\text{PSN}$  system results in higher ordering degree of the crystals at intermediate concentrations in comparison with the boundary ones in agreement with our experimental findings. Thus the same regularities of ordering are valid for solid solutions of both 1:1 and 1:2 ternary perovskites.

Though the ordered domain sizes are similar ( $\sim 50$  nm) in both systems, PSN-PST crystals with  $x > 0.3$  display a sharp permittivity peak while a relaxor-like dielectric behavior is observed for PMN-PSN compositions with  $y < 0.6$ . At  $y > 0.6$  the excitation energy, determined from the Vogel-Fulcher relation, experiences a large drop and remains approximately constant above this point. The shape of the dielectric permittivity  $\varepsilon$  curve at this point also changes substantially, i.e. a sharp step appears on it somewhat below the temperature  $T_m$  of the  $\varepsilon(T)$  maximum. These results are similar to those obtained earlier for annealed PMN-PSN ceramics [1] and are consistent with the random-site model of 1:1 B-site cation ordering in 1:2 ternary Pb-containing perovskites. In order to understand these results deeper we have developed a model according to which, at  $y \sim 0.6$ , the kind of the polar region changes from PMN (or Mg)- related to PSN (or Sc)- related.

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## Properties of hexagonal ScN from first-principles<sup>†</sup>

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Local-density approximation calculations are performed to predict structural, dielectric, piezoelectric, electronic and vibrational properties of hexagonal ScN. The lowest-in-energy 4-atom-per-cell hexagonal structure is found to be non-polar and nearly five-times coordinated<sup>1</sup>. Interestingly, this structure is very similar to the metastable phase predicted to occur in MgO<sup>2</sup>. This phase may thus exist in many other compounds and hence may have been overlooked in earlier works. Furthermore, applying an external stress to this structure results in several remarkable ferroelectric-like features, e.g. phase transition from paraelectric-to-pyroelectric structures, condensation of phonon modes and enhancement of electromechanical responses. Moreover, hexagonal ScN also reveals some semiconductor-like features, e.g. it allows for a band-gap engineering. This unusual compound can thus be thought as a bridge between ferroelectrics and semiconductors, and thus opens many new possibilities.

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## A Site Substitution and Local Structure in Ferroelectric Perovskites

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Complex perovskite compounds of the form  $(AA')(BB')O_3$  and  $A(BB'B'')O_3$  have been found to possess piezoelectric, dielectric, and electro-optical properties that show promise in a variety of applications. Many of these properties are strongly controlled by and correlated with the local disorder in the  $A$  and  $B$  sites. We study properties of the Pb-based, solid-solution transition-metal oxides  $(A_x\text{Pb}_{1-x-y}A'_y)\text{TiO}_3$  (“ $A$ ” stands for lanthanum or any other trivalent transition metal, “ $A'$ ” stands for alkali) using first-principles density functional theory. In an analogy with the well-known complex piezoelectric material PZT, we investigate the local structures that can result from the ionic size and valence differences between the lead, the  $A$ , and the  $A'$  atoms. The effect of alkali and rare-earth substitutions on the local structure will be discussed. The possibility of relaxor behavior due to the locally fluctuating valence states at the  $A$  sites will be investigated.

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## Particle transport along domain walls: superhighways or parking lanes?

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After the discovery of superconducting twin walls in ferroelectric WO<sub>3</sub>, the general issue of particle transport along domain walls has been investigated experimentally and by computer simulation. Premelting along twin walls and APBs were found to occur in all ferroelastic materials investigated. Mott transitions and other electronic phase transitions within the twin walls could be described analytically by bi-quadratic order parameter coupling bearing in mind that the characteristic wall thickness is in the order of a few nanometers even at low temperatures. Surfaces interact strongly with wall trajectories. Walls perpendicular to the surface show elastic softening of the wall core and hardening at the wall rim. The hardening decays exponentially with increasing distance from the site of the wall-surface intersection. Chemical potentials appear to scale as the square of the ferroelastic order parameter. When two walls form needle domains we find that the needle tip is attracted to the surface so that the more common configuration consists of needles with their base on the surface and the tips pointing away from the surface. The atomic structure of the core of the wall can be much more complex than that of the paraphase, although in all cases we found a tendency of the centre of the wall to relax towards a structure similar to that of the paraphase. An extreme example seems to be the Dauphine wall in quartz where the wall is determined entirely by ellipsoidal Si-O rings which allow a best match between the two adjacent domains. The ring structure is not hexagonal, however, but highly distorted monoclinic with ring diameter smaller than those of the bulk material. This leads to significant trapping of ions inside the walls when transport is attempted along the crystallographic *c* axis. Transport is increased along other directions. Sandwich configurations which alternating 3 order parameters were found in other ring structures. In perovskite structures transport is mainly enhanced along the twin walls, examples will be discussed.

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## Polarization Rotation and Monoclinic Phase in Relaxor Ferroelectric PMN-PT Crystal

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A monoclinic phase is evidenced between rhombohedral and cubic phases in a  $\langle 111 \rangle$ -cut single crystal PMN - 33 % PT from observation of domain structures. Near 360 K the structure begins to distort from the rhombohedral toward the tetragonal phase through monoclinic domains (probably  $M_A$ -type but perhaps  $M_B$ -type). However, the present  $\langle 111 \rangle$ -cut crystal seems to disfavor the tetragonal phase and persists in the monoclinic phase up to  $T \sim 420$  K, where the cubic phase begins to develop. Temperature-dependent orientations of optical indicatrices of domains indicate polarization rotations within the monoclinic planes. In addition, a previous electric-field-cooled process enhances a long-range transformation. At room temperature, with increasing E-field along  $[111]$ , the crystal undergoes a successive phase transformation via polarization rotations (perhaps  $M_A$ -type), i.e. rhombohedral  $\rightarrow$  tetragonal (associated with  $90^\circ$ -domain walls)  $\rightarrow [111]$  rhombohedral. As E-field decreases, very different domain patterns appear (as compared with those with increasing field) that indicates a strong hysteresis relation between E-field and strain.

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## **Ferroelectric Nanotubes**

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I report the invention of ferroelectric nanotubes via a misted sol-gel deposition of charged droplets (-5e average charge) that is akin to the original Millikan oil-drop experiment. Data, particularly SEM results, will be presented on SBT, although BaTiO<sub>3</sub> and PZT can be made in a similar fashion. The nanotubes are in the form of hexagonal ordered arrays of a few thousand tubes. Inside diameters can be made from 0.1 microns to about 3.0 microns; depth is >60 microns (giving a maximum aspect ratio of 600:1); and wall thickness is 0.2-1.4 microns. These new devices can be used as free-standing voltage-tunable photonic arrays. Because they are piezoelectric, they can also be used as ink-jet printers, where they are capable of producing sub-picoliter droplet delivery (state of the art is the Seiko-Epson 1.0 picoliter system, which can write 1.0 micron lines for lithography-free printing of chips); and they provide a factor of  $\times 10$  in aspect ratio for Si DRAM trenching, where typical values are (Infineon) 0.1 micron diameter  $\times$  6.0 microns deep (60:1 aspect ratio). This extra factor of  $\times 10$  in capacitance per bit for DRAMs should be of immediate commercial interest, since dep-rates and throughput are very rapid.

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## Electronic structure of perovskite transition metal oxides by quantum Monte Carlo approaches

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We present a report on recent progress in application of quantum Monte Carlo (QMC) methods to accurate electronic structure calculations of ferroelectric transition metal oxides. There are three major aspects of these methods.

(i) Construction of accurate many-body wave functions using orbitals from one-particle approaches such as Hartree-Fock and hybrid DFT functionals like B3LYP. (ii) Efficient calculations of excitation energies both in variational and diffusion QMC. (iii) An attempt to calculate small energy differences such as subtle features on total energy surfaces related to ferroelectricity. We compare the computational demands and accuracy of these calculations compared to those for sp-systems.

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**Non-Debye type relaxator study with Cole-Cole plots in  
Ce<sup>3+</sup> doped Sr<sub>0.61-x</sub>Ba<sub>0.39</sub>Nb<sub>2</sub>O<sub>6</sub>Ce<sub>x</sub> (x=0, 0.0066)**

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The dielectric behaviour of materials under external AC field has been the focus of numerous papers, in view of its high scientific and technological importance. Measurements are made in a wide of frequencies and temperatures for many types of materials. Strontium-Barium Niobate, Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub> type formula (abbreviated as SBN), is a promising material due to its very attractive piezoelectric, electrooptic, acoustooptic, photorefractive, non-linear optic properties. The dielectric properties of Sr<sub>0.61-x</sub>Ba<sub>0.39</sub>Nb<sub>2</sub>O<sub>6</sub>Ce<sub>x</sub> (x=0, 0.0066) were studied as a function of temperature and frequency. The temperature dependence of dielectric measurements revealed a ferroelectric phase transition at 360 K (x=0) and 340 K (x=0.0066). The frequency dependence of dielectric constant, tangent loss factor, dielectric relaxation and activation energy were analysed in frequency range from 0.1 kHz to 10000 kHz. Cole-Cole plots technique was also used to examine the existence of single relaxator in the vicinity of phase transition. A non-Debye type single (x=0) and double (x=0.0066) dielectric relaxation mechanism were observed around phase transition temperature, which was not reported by using Cole-Cole plots technique so far.

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# Atomistic model potential for $\text{PbTiO}_3$ fitted to LDA and GGA first-principles results

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An atomistic model with parameters determined completely from first-principles results could be used to study the effects of temperature and composition on piezoelectric and ferroelectric properties. However, the reliability of the simulated results will depend on the precision that the model reproduces the relevant physics obtained from first-principle calculations. Moreover, the results could be affected by the accuracy of the exchange-correlation functional (LDA or GGA) used to generate the input data.

In the present work we determine two different set of shell-model parameters for  $\text{PbTiO}_3$  by fitting first-principles results. The first model was fitted to LDA values of total energies and atomic forces, while in the second case GGA-LAPW results were used. The different configurations used in the fitting include various distortions as well as atomic displacements according to the soft mode and lattice strains. Also, we used in both models the same data to fit effective charges, phonon frequencies and eigenvectors at different  $q$  points along high symmetry directions in the cubic cell [1].

First-principles results show that the tetragonal structure is more stable than the rhombohedral one at all volumes. In LDA, the ground state presents a  $c/a$  distortion of 1.04 and a volume 5% smaller than the experimental one, while in GGA  $c/a=1.20$  with a 10% bigger volume. At the experimental volume,  $c/a=1.12$  in LDA, and 1.09 in GGA. As a consequence, the two fitted models have different values for the parameters. In each case, the model presents a good agreement with the input data at the experimental volume. However, the ground state in both cases are very sensitive to the volume. The model fitted to LDA has a rhombohedral ground state, and it only become tetragonal with  $c/a=1.12$  at a negative pressure of -1.85 GPa. On other hand, the model fitted to GGA is tetragonal with  $c/a=1.18$ , but it becomes rhombohedral with a small decrease of  $V$ . Molecular dynamic simulations in both models present also similar characteristics: a strong dependence with the temperature of the tetragonal distortion, and a transition from tetragonal to cubic at 800 K. It is not clear that the dependence of the tetragonal distortion with temperature is only a model related problem because the  $c/a$  distortion strongly depends with volume in first principle calculations.

[1] Ph.Ghosez, E.Cockane, U.Waghmare and K.Rabe, Phys. Rev B, **60**, 836, 1999.

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## A new mechanism for ferroelectricity and a new ferroelectric with an old mechanism

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First, we describe the first-principles identification of a new mechanism for ferroelectricity which occurs in hexagonal perovskite manganites such as  $\text{YMnO}_3$ . The ferroelectric phase is characterized by a rotation of the  $\text{MnO}_5$  polyhedra, which, combined with the unusual yttrium co-ordination and the layered, triangular network of  $\text{MnO}_5$  bipyramids, leads to a net electric polarization. The usual changes in chemical bonding associated with ferroelectric phase transitions do not occur, and so the usual indicators of ferroelectric instability, such as anomalies in Born effective charges on the active ions, do not hold. Since the  $Z^*$ s are not large, we anticipate a lower sensitivity of the ferroelectric state to domain structure and boundary conditions than in conventional ferroelectrics.

Second, we predict a new ferroelectric,  $\text{BiAlO}_3$ , in which the mechanism for ferroelectricity is the well-established stereochemical activity of the lone pair on the A-site cation. However in contrast to well-known A-site active ferroelectrics such as  $\text{PbTiO}_3$ , the B-site in  $\text{BiAlO}_3$  does not show a second-order Jahn-Teller distortion. Therefore  $\text{BiAlO}_3$  is an ideal model compound for distinguishing A- and B-site contributions to ferroelectricity.

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# **PbTiO<sub>3</sub> at Finite Temperature: An Ab-initio Molecular Dynamics Study**

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PbTiO<sub>3</sub> is a prototypical ferroelectric material that exhibits a structural phase transition from a tetragonal to a cubic phase at  $T = 763$  K. This is a soft mode driven, predominantly displacive, phase transition. In this paper, we study the behavior of PbTiO<sub>3</sub> at finite temperature by ab-initio molecular dynamics simulations. In this approach classical mechanics is used to describe nuclear dynamics, while the interatomic potential is generated on the fly from the ground state of the electrons within density functional theory. In our implementation we use the PBE generalized gradient approximation for the exchange and correlation energy and potential, and use plane waves and ultrasoft pseudopotentials to describe the valence electrons. Fluctuations of volume and shape of the simulation cell are included by means of Parrinello-Rahman constant pressure molecular dynamics simulations. Extensive convergence studies based on static calculations indicate that a  $3 \times 3 \times 3$  supercell containing 135 atoms, with a single  $k$ -point sampling, is sufficient to represent accurately the  $T = 0$  energetics of this material. Although computationally demanding, ab-initio molecular dynamics simulations for PbTiO<sub>3</sub> using a  $3 \times 3 \times 3$  cell are feasible with current computational methodologies. We report results of simulations at temperatures that are both below and above the ferroelectric phase transition. We discuss, in particular, how phonon softening occurs with temperature and how thermal expansion affects the results. This work was supported by the Office of Naval Research.

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## Anomalous enhancement of tetragonality by negative pressure in $\text{PbTiO}_3$

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The dramatic improvement of electromechanical properties obtained for certain Pb-based perovskite alloys has led researchers to explore new ways of obtaining other compounds with similar properties. One desirable property is a large strain, i.e., a large  $c/a$  ratio in the tetragonal phase. Using first-principles calculations, we have found that a large tetragonal strain can be induced by application of a *negative* hydrostatic pressure in  $\text{PbTiO}_3$ , one of the simplest compounds in this class of materials. The structural parameters such as cell volume and atomic displacements are found to change rapidly near a critical pressure, displaying a “kinky” behavior suggestive of proximity to a phase transition. Parallel calculations for  $\text{BaTiO}_3$  show that the same effect is also present there, but at much higher pressure. We investigate this unusual behavior of  $\text{PbTiO}_3$  and discuss its possible interpretation in terms of a phenomenological description using a reduced set of relevant degrees of freedom. Although the application of negative pressure is not feasible experimentally, our theoretical study may provide useful insights into the structural instabilities of  $\text{PbTiO}_3$ , and may ultimately help suggest other, more practical avenues leading to enhanced tetragonality in  $\text{PbTiO}_3$  and related compounds.

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# Structural synchrotron x-ray studies of anti-ferrodistortive nanodomains in PMN relaxor

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Synchrotron x-ray scattering studies were applied to single crystals of lead magnesium niobate  $Pb(Mg_{1/3}Nb_{2/3})O_3$  (PMN) and  $[PbMg_{1/3}Nb_{2/3}O_3]_{1-x}[PbTiO_3]_x$  (PMN-xPT) with Ti doping  $x \leq 0.3$ , which are classic examples of cubic Perovskite relaxor ferroelectrics. Dielectric behaviors in PMN-PT were explained by newly developed Spherical-Random-Bond-Random-Field model (SRBRF) as a result of competition between randomly occurring dynamic ferroelectric and anti-ferroelectric fluctuations in conjunction with the presence of disorder. This competition leads to gradual freezing into a glass-like state reminiscent to magnetic spin-glasses, while the average crystal structure is indistinguishable from cubic at all temperatures. Extensive experimental evidence reported in the literature suggests that ferroelectric fluctuations have rhombohedral symmetry in PMN. On the other hand, no clear experimental evidence exist for anti-ferroelectric fluctuations.

Anti-ferroelectric ordering is established by correlated atomic displacements which produce dipole moments with anti-parallel arrangement throughout the crystal. Studies of anti-ferroelectric nanodomains with techniques sensitive to electric dipoles are challenging, since the net polarization for each nanoregion is zero. However, structural differences between the nanoregions and cubic host lattice can be studied by analytical techniques such as electron, neutron and x-ray scattering. Third generation synchrotron x-ray sources, for example, may provide incident photon flux  $\sim 10^9$  times of that of the conventional x-ray sources, thereby providing an excellent tool to study very weak structure fluctuations.

From diffraction point of view, each type of fluctuations contributes intensity to the different parts of the reciprocal space. Diffuse scattering from ferroelectric fluctuations is mainly concentrated near fundamental Bragg reflections while anti-ferroelectric fluctuations produce diffuse superlattice reflections ( $\alpha$  spots) at the Brillouin zone boundaries as a result of the unit cell doubling.  $\alpha$  spots are extremely weak and were originally observed with electron diffraction, however they have never been observed with laboratory x-ray sources. In related Perovskite single crystals, such as fully ordered  $Pb(In_{1/2}Nb_{1/2})O_3$  (PIN), temperature dependence of the  $\alpha$  spots was reported to mark anti-ferroelectric phase transition, which suggests similar anti-ferroelectric origins for the  $\alpha$  spots in PMN.

Intensities of the strong anisotropic diffuse scattering ridges in PMN along  $\langle 1\bar{1}0 \rangle$  reciprocal directions overlap with intensities of the  $\alpha$  spots. We were able to effectively separate two different contributions along  $\langle 1\bar{1}0 \rangle$  type directions and study their temperature dependence independently in the wide temperature interval 15 – 800K. We found that Intensities of the anisotropic diffuse scattering ridges are temperature independent in the whole temperature interval for  $q \geq 0.1$  reciprocal lattice units (r.l.u). Freezing phase transition has been identified in PMN near  $T_f = 220$  K from the temperature dependence of the integrated intensity of the  $\alpha$  spots. It was found that the freezing temperature  $T_f$  coincides with the phenomenological Vogel-Fulcher temperature obtained from the macroscopic dielectric measurements.

The size of the anti-ferroelectric fluctuations was estimated to be about 30 Å from the width of the  $\alpha$  spots, which was found temperature independent below  $T_f$ . Contribution of the Pb atoms to the structure factor of the  $\alpha$  spots was inferred from anomalous scattering results obtained by tuning the energy of the incoming x-ray radiation near  $Pb L_{III}$  absorption edge to highlight the scattering contrast from the atoms of interest. Comparison of the observed and calculated integrated areas of the  $\alpha$  spots below freezing temperature ( $\sim 220$  K) brought us to conclusion that magnitude of correlated  $\langle 110 \rangle$  Pb displacements is also temperature independent below  $T_f$  and estimated to be  $\sim 0.3$  Å from structure factor refinement. Dramatic increase in the intensity of the  $\alpha$  spots below  $T_f$  we attributed to rapid nucleation of the anti-ferroelectric domains without growth, which competes with similar percolation type nucleation of the ferroelectric nanodomains.

To summarize, temperature dependent synchrotron x-ray diffraction studies of PMN-PT single crystals confirmed the existence of anti-ferroelectric fluctuations produced by correlated atomic displacements using state-of-the art experimental facilities. Detailed quantitative structure factor analysis of the corresponding superlattice reflections has been performed for the first time.

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## Condensation and Slow Dynamics of Polar Nanoregions in PMN, PZN and PZN-PT

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It is now well established that the unique properties of relaxor ferroelectrics are due to the presence of polar nanoregions (PNR). In this talk, we present recent results from Raman and Neutron scattering measurements on single crystals of PMN, PZN and PZN-PT. These results provide information on the condensation of the PNR and on their slow dynamics, directly through the Central Peak and, indirectly, through their coupling to transverse phonons. A comparative analysis allows identification of three phases in the evolution of the PNR with decreasing temperature: a purely dynamic phase, a quasi-static phase with reorientational motion and a frozen phase. A model is also proposed, based on a prior study of KTN, which explains the special behavior of the transverse phonons (TO and TA) in terms of their mutual coupling through the rotations of the PNR.

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## Phase Transformation vs. Monoclinic Rotations in $\langle 102 \rangle$ -cut PMN-PT Crystal

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Recent results [J.-M. Kiat et al., Phys. Rev. B **65**, 064106 (2002); B. Noheda et al., Phys. Rev. B **66**, 054104 (2002)] showed that the monoclinic phase ( $M_C$ -type) appears below room temperature in unpoled ceramics and powder of PMN-PT for compounds near morphotropic phase boundary (MPB). One may ask whether the monoclinic phase (M) or various phase coexistences (such as rhombohedral/monoclinic) are intrinsic, or are merely due to spatial phase segregation, or defect-induced strains of a given phase away from the ideal structure for that phase. In this report, temperature-dependent polarizing microscopy was used to investigate various domain phases on both unpoled and poled  $\langle 102 \rangle$ -cut PMN-31 % PT single crystal. By using relations of optical indicatrices and extinction, the unpoled PMN-31 % PT crystal was evidenced to possess a rhombohedral phase at room temperature. As temperature increases, the extinction angle doesn't exhibit apparent change until  $\sim 350$  K, indicating that the crystal keeps a rhombohedral phase mostly below  $\sim 350$  K. Above  $\sim 350$  K, the extinction angle begins to rotate through the monoclinic phase and then reach the tetragonal phase mostly near 400 K. Near 410 K, the crystal transforms into the isotropic cubic phase. In addition, E-field (along the  $[102]$  direction) dependent domain structures have also been observed at room temperature. The optical indicatrices of domain matrix begin to rotate at  $E > 4.5$  kV/cm via various monoclinic polarizations. However, the crystal doesn't exhibit totally extinction even under an electric field of  $E=40$  kV/cm, indicating field-induced single domain has not been reached. The domain structures show a strong hysteresis behavior during processes of increasing and decreasing E-field.

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## Ab-Initio Molecular Dynamics in a Finite Homogeneous Electric Field

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We treat homogeneous electric fields within density functional calculations with periodic boundary conditions. The ground state is found by minimizing a nonlocal energy functional depending on the applied field. When applied to a crystalline system, this functional preserve the translational symmetry. This approach is included within an *ab initio* molecular dynamics scheme. The reliability of the method is demonstrated in the case of bulk MgO for the Born effective charges, and the high- and low-frequency dielectric constants. We evaluate the static dielectric constant by performing a damped molecular dynamics in an electric field, and avoiding the calculation of the dynamical matrix. Application of this method to vitreous silica shows good agreement with experiment and illustrates its potential for systems of large size.

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## Topology of Polar Nanoregions in Relaxor Ferroelectrics

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Topology of polar nanoregions in relaxors and its change with temperature or under the field is one of the most important characteristics, determining such practically important phenomena, as aging, fatigue etc. In relaxors and similar compounds topology and other spatial characteristics of polar nanoregions are determined by many factors such as composition, anisotropy (cubic or uniaxial), and influence of the applied electric field. Depending on this parameters either glassy state with smooth variation of the polarization through the crystal or the nanodomain state with well-defined homogeneous nanoregions can be formed.

We have performed detailed study of Bragg and diffuse scattering of neutrons and X-rays in several compounds under different conditions.

- In pure PMN and PMN/6%PbTiO<sub>3</sub> (PMNPT6) cooled without electric field no indications of the formation of nanodomains was, although at freezing temperature topology change was found that can be described in terms of increase of fractal dimension.
- In PMNPT10 and PMNPT25 below freezing temperature nanodomain or mixed ferroglass state is formed.
- In PMN cooled under the electric field and then heated back topology of polar nanoregions is substantially different from that in “virgin” or annealed PMN and is more consistent with nanodomain description.
- In uniaxial relaxor Sr<sub>1-x</sub>BaxNb<sub>2</sub>O<sub>6</sub> (SBN) nanodomain state is formed on cooling, that is strongly affected by an applied electric field.

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## Phase diagrams and diffusion in multicomponent oxides from first principles

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Optimizing or tailoring properties of technologically important oxides is often done by doping the material with specific elements. On the other hand, the ability of some alkali transition metal oxides to readily undergo large concentration variations electrochemically is exploited in battery applications. In both cases, compositional modifications may result in the destabilization of a desired oxide crystal structure. Whether or not an oxide phase decomposes upon modification of its composition depends on the thermodynamic driving forces and the kinetic barriers along the decomposition path. In this respect, a phase diagram serves as a useful map, indicating the regions in composition and temperature space in which different phases are thermodynamically stable. Ionic diffusion coefficients are often invaluable in understanding the rates with which phase transformations involving cation redistribution occur. In this talk, we will describe methods to calculate phase diagrams and diffusion coefficients in multicomponent oxides with substitutional disorder from first principles. This involves a combination of accurate first principles total energy methods with lattice model Hamiltonians and Monte Carlo simulations. We will present results on studies of phase stability and diffusion in lithium transition metal oxides and Yttria doped Zirconia.

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## Role of Microtwins in Poled Oriented Single Crystals of PMN-PT

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Structural and property investigations of poled oriented single crystals of various compositions of PMN-PT have revealed tetragonal and rhombohedral microdomains, which exist within monoclinic macrodomains. We show evidence by reciprocal space mapping, transmission electron microscopy and macroscopic property investigations. We offer the alternative model that monoclinic symmetry is a natural consequence of stress-accommodating tetragonal and rhombohedral structural microtwins that have polarization. We will show that the lattice parameters of the monoclinic phases (and subsequent changes with temperature, stress and electric field) are invariant to the elastic compatibility condition. The monoclinic lattice parameters will be shown to be equal to those predicted by applying the twinning rules to conformally miniaturized rhombohedral and tetragonal microdomains.

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## First-principles study of the electrooptic effect in ferroelectric oxides

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Ferroelectric oxides are well known for their unusual dielectric and non-linear optical properties. For example, their large electrooptic coefficients are at the origin of various applications. Nowadays, these materials are widely used in devices like modulators for fiberoptic communications systems. Moreover, because the photorefractive effect strongly depends on the electrooptic coefficients, they are also considered as serious candidates for holographic data storage<sup>1</sup>.

We used first-principles calculations performed within the Kohn-Sham density functional theory to investigate the electrooptic effect in ferroelectric  $\text{ABO}_3$  compounds. This study is based on a perturbative expansion of the total energy thanks to the  $2n + 1$  theorem and the modern theory of polarization. Our aim was to identify the microscopic origin of the large electrooptic coefficients.

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## Pressure as a Probe of the Physics of Compositionally-Substituted Quantum Paraelectrics: SrTiO<sub>3</sub>\*

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Understanding the dielectric properties and phase behavior resulting from chemical substitution in the classic quantum paraelectrics (QPE's) SrTiO<sub>3</sub> and KTaO<sub>3</sub> is a subject of current interest. By tuning the delicate balance between short-range and Coulombic forces in these systems, hydrostatic pressure has been shown to provide much insight into the underlying physics. In this presentation we discuss the dielectric response versus pressure, temperature and dc electric field for two substituted single crystals of SrTiO<sub>3</sub>: (a) <sup>18</sup>O exchanged SrTi<sup>18</sup>O<sub>3</sub> [STO18] and (b) lightly doped Sr<sub>1-x</sub>Ca<sub>x</sub>TiO<sub>3</sub> [SCT(0.007)] with x=0.007. The <sup>18</sup>O atoms in STO18 reduce both the quantum fluctuations of the TiO<sub>6</sub> octahedra and the frequency of the soft phonon mode, leading to a FE state via a first-order transition with T<sub>c</sub> ~ 24 K at ambient pressure. T<sub>c</sub> decreases very rapidly under pressure with an initial slope of ~20 K/kbar, reaching the quantum displacive limit (T<sub>c</sub> = 0 K) near 0.7 kbar. In the case of SCT(0.007), fluctuating polar nanodomains surround the off-center Ca dopants and grow in size as the correlation length for dipolar interactions in the SrTiO<sub>3</sub> host increases with decreasing temperature. Ultimately, the fluctuations slow down and the nanodomains "freeze" into a relaxor state with T<sub>m</sub> ~ 18 K; pressure reduces T<sub>m</sub> with an initial slope of ~35 K/kbar. Both the FE transition in STO18 and the relaxor state of SCT(0.007) are completely suppressed below 1 kbar and a QPE state emerges. In both crystals a dc electric field counteracts some of the effects of pressure, and the interplay between these variables provides additional insight into the properties. Similarities and differences between the two systems will be discussed. The unusually large effects of pressure and bias field emphasize the very delicate balance between competing interactions in both systems.

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## Epitaxial BiFeO<sub>3</sub> Multiferroic Thin Film Heterostructures

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Dramatically enhanced polarization responses in heteroepitaxially constrained thin films of the ferroelectromagnet, BiFeO<sub>3</sub> are reported. Structure analysis indicates that the crystal structure is monoclinic in contrast to bulk, which is rhombohedral. The films display spontaneous polarization at room temperature, of about 50-60  $\mu\text{C}/\text{cm}^2$ , which is almost an order of magnitude higher than the reported bulk value of 6.1  $\mu\text{C}/\text{cm}^2$ . The large polarization in the thin films is confirmed by first-principles calculations and found to originate from large relative displacements of Bi, Fe, and O sublattices. Piezoresponse scanning force microscopy yields a  $d_{33} \sim 70 \text{ pm/V}$ , which has never been reported before. The films also exhibit dramatically enhanced magnetism (150 emu/cc for a 70 nm film) compared with bulk. Thickness dependence of both ferroelectricity and magnetism confirms the relationship between the enhanced properties and heteroepitaxial strain.

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## Noise and Aging Studies of Relaxor Ferroelectrics

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We have combined aging [1] and noise[2] techniques to elucidate the types of frozen order formed in the relaxor regime. We find that in PMN, PMN-0.1PT, and PLZT aging deep in the relaxor regime shows several features characteristic of spinglasses, including multiple independent susceptibility 'holes' formed at different aging temperatures. This effect requires complex cooperative glassy freezing of many local units. However, the field scale required to disrupt the aging is anomalously high compared to spinglasses, if a nanodomain is the unit corresponding to a spin. Barkhausen noise results imply cooperative moment changes involving several nanodomains near  $T_g$ , but much smaller steps below  $T_g$ . This result suggests that kinetic barriers increase at  $T_g$  without increasing coupling among nanodomains. Together, these results suggest that in prototypical relaxors the glassy state is not formed by nanodomains, although it affects their dynamics, but rather by smaller units. We tentatively propose that the canted components of the local polarizations (found in scattering experiments [3]) are analogous to the x-y spins in a reentrant spinglass. The first tested prediction of this new picture is that spinglass-like aging effects would be absent in the uniaxial 'relaxor' SBN. Such effects do vanish well below  $T_g$  in SBN, although some are present near  $T_g$ .

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## Weighted Density Approximation (WDA) Calculations for Ferroelectric Materials

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Although LDA and GGA are extraordinarily successful, they fail to predict certain properties accurately, e.g., the equilibrium volume, band gaps and the dielectric constant. The weighted density approximation (WDA), which incorporates nonlocal information through a model exchange-correlation (xc) hole, was proposed to fix the drawbacks of LDA [1,2,3,4]. We used Plane-wave basis, Perdew-Wang pair-distribution functional [2], and shell partitioning [1,4], within which the valence-valence interaction is treated with WDA, while core-core and core-valence interactions are treated with LDA. We calculated the ground-state properties of  $\text{KTaO}_3$ ,  $\text{KNbO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$  and PMN. Comparing with LDA, WDA significantly improves the equilibrium volumes of these ferroelectric materials for the cubic state, but it severely overestimates the soft-mode instabilities of rhombohedral  $\text{BaTiO}_3$  and tetragonal  $\text{PbTiO}_3$ . Another subtle issue is that whether or not including Pb 5d states in valence dramatically changes the WDA equation-of-state of cubic  $\text{PbTiO}_3$ . Improvements will be discussed.

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## Multinuclear Single and Multiple Quantum MAS NMR Studies of Perovskite Relaxor Ferroelectrics

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Multinuclear ( $^{207}\text{Pb}$ ,  $^{45}\text{Sc}$ ,  $^{93}\text{Nb}$ ) NMR has been used to investigate the local structure and cation disorder in solid solutions of  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ :  $x\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ , as a function of concentration. These relaxor ferroelectrics have been well characterized by X-ray and dielectric response measurements(1). The  $^{93}\text{Nb}$  MAS line shapes were assigned to species with different arrangements of the nearest B-cation neighbors. It was necessary to include distributions of the electric field gradient parameters and dispersions in isotropic chemical shifts; these were estimated from the data. The relative intensities of each spectral component were analyzed and the data strongly support the modified Random Site model. To explain NMR intensities and to validate the model, Monte Carlo simulations were performed(2).

In this poster,  $^{93}\text{Nb}$  3QMAS spectra are presented and analyzed for concentrations  $x = 0, 0.1, 0.2, 0.6, 0.7$  and  $0.9$ , at high magnetic field (19.6T) and fast spinning speed (35.7 kHz). The unique high resolution of the two-dimensional 3QMAS spectra enables unambiguous and consistent assignments of spectral intensities of seven narrow peaks and two broad peaks to specific nearest B-site neighbor configurations. NMR parameters have been calculated for most of these local cation configurations. Most notably, it is now possible to isolate the isotropic shift from the quadrupole coupling product, and to reliably extract their separate distribution widths. Ordinary MAS spectra are not well enough resolved for this purpose.

In distinct contrast to  $^{93}\text{Nb}$ ,  $^{45}\text{Sc}$  MAS spectra are narrow and no fine structure is resolved, even at 19.6T. Nevertheless, it is possible to deconvolute and fit the line shapes by a weighted sum of three or four Gaussian-Lorentzian peaks, whose relative intensities change in a regular manner with increasing scandium content. Implications of these results for models of local B-site cation disorder will be presented.

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